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EVALUATION OF THE FOUR ELASTIC CONSTANTS OF SOME CUBIC CRYSTALS

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1. Introduction

The mathematical theory of elasticity in its generally accepted form derives from a memoir by A. L. Cauchy presented to the Academy of Sciences at Paris in 1822. The analytical specification of the strains and stresses in elastic solids adopted in that theory expresses the strains in terms of the differential displacements of neighbouring points in the solid and the stresses in terms of the tractive forces on infinitesimal areas in the same location. The theory, however, does not make use of these representations with complete generality, but following Cauchy, adopts them in modified forms on the basis of arguments put forward by him and considered as authoritative ever since. But when one examines those arguments critically, they are found to be indefensible. This is particularly clear in regard to the representation of strains. In the most general case, we have nine components of strain, but Cauchy reduced their number to six by eliminating movements which he identified with rigid body rotations. Actually, however, the components thus eliminated are not rigid body rotations, but differential rotations which are of the same nature as those appearing in the deformation of solids by torsion or flexure and hence, their elimination is not justified. Then again, Cauchy's reduction in the number of the stress components from nine to six is based on the idea that the angular momenta of the tractions taken about each of the co-ordinate axes and summed up should cancel out. But since the stresses are assumed to be in the nature of tractive forces and defined in terms of their magnitudes over infinitesimal areas, they have to be considered as acting on volume elements which are small enough to be regarded as particles and hence no consideration of angular momenta is called for. The reduction in number of the components of stress from nine to six has therefore no justification. Indeed, when once it is admitted that we have to retain all the nine components of strain, a similar step in regard to the components of stress follows inevitably.

In a recent paper (Raman and Viswanathan, 1955) the consequences of adopting the representations of stress and strain in elastic solids in their most general form have been discussed in detail. It has been shown in that

paper that Cauchy's assumptions result in restricting the cases which fall within its scope to homogeneous strains properly-so-called. The more general case of heterogeneous strains, including especially all cases of wave-propagation and static deformations in the nature of torsion and flexure, lie outside its scope. Nevertheless, the mathematical theory of elasticity has actually been applied to these cases and formulæ have been obtained and the constants appearing in them have been evaluated experimentally. For example, the results of experimental studies with cubic crystals have been expressed in terms of three constants usually designated as C_{11}, C_{12} and C_{44} respectively. On the other hand, the more general theory shows that four constants designated as d_{11}, d_{12}, d_{44} and d_{45} are needed for the classes O*h* and T*d* of the cubic system. Hence, by an examination of the experimental data for those cubic crystals of the O*h* and T*d* classes which have been investigated with adequate precision by different methods, it should be possible to decide whether those data are expressible in terms of three constants only, or whether four constants are actually needed. It is the object of the present paper to present the results of such an examination.

2. SOME GENERAL REMARKS

The determination of elastic constants of crystals can be made independently by static and dynamic methods. In the former case we naturally deal with the elastic constants under isothermal conditions and in the latter case under adiabatic conditions. The dynamic methods depend upon the determination of velocity of propagation of high-frequency waves of different types in the solid. Many of the recent determinations of the elastic constants of crystals have been made by these methods and it would seem that a high degree of precision has been attained in the resulting data. We shall accordingly make use of them in the evaluation of the elastic constants of the respective materials.

The classical expression for the velocity of propagation in a cubic crystal in the older theory is given by equations of the type

$$\rho v^2 A^x = A^x \{C_{11} l^2 + C_{44} (m^2 + n^2)\} + (C_{12} + C_{44}) (A^y lm + A^z ln)$$

while in the corrected theory it is given by equations of the type

$$\rho v^2 A^x = A^x \{d_{11} l^2 + d_{44} (m^2 + n^2)\} + (d_{12} + d_{45}) (A^y lm + A^z ln)$$

Thus in reducing the experimental data we make the following identifications:

$$d_{11} = C_{11};\ d_{44} = C_{44} \text{ and } (d_{12} + d_{45}) = (C_{12} + C_{44}).$$

It will be seen at once that if $d_{44} = d_{45}$, then the two theories lead to identical results.

Whereas in the older theory, if the wave-velocities had been measured for a sufficient number of directions the data resulting would suffice to determine the constants C_{11}, C_{12} and C_{44}, in the present theory it only enables us to evaluate the three quantities d_{11}, d_{44} and $(d_{12}+ d_{45})$. Thus, at least one additional determination is needed by static methods yielding values for a different linear combination of the four constants. The most appropriate determination appears to be the bulk modulus the expression for which under the older theory is $(C_{11}+ 2C_{12})/3$, whereas in the new theory it is $(d_{11}+2d_{12})/3$. While determinations of the bulk modulus are not easy, there is reason to believe that a degree of precision adequate for our present purpose has been reached in the measurements made and reported from Bridgman's laboratory at Harvard. It is obvious that to utilize these data in conjunction with the determinations by the dynamic methods, it is necessary to assume that we are dealing in both cases with the same material and under the same physical conditions. Such an assumption would appear *prima facie* justifiable in the cases considered in the present paper, *viz.*, crystallised solids of very simple chemical composition. The correctness of the assumption is reinforced by an intercomparison of the elastic constants determined by dynamic methods and reported by different authors from different laboratories. In general, these values do not differ more than can reasonably be ascribed to inevitable uncertainties in the experimental determinations.

Some further remarks are also necessary in this connection. Since the experimental values for the compressibility refer to isothermal conditions it is necessary to correct them to obtain its value under adiabatic conditions in order that a comparison might be possible with the adiabatic constants determined by dynamic methods. This correction is effected making use of the well-known formula

$$\chi_{iso} - \chi_{adia} = \frac{9\alpha^2 T}{\rho C_p}$$

where χ represents the compressibility, α the coefficient of linear expansion of the substance, T the absolute temperature, ρ the specific gravity of the solid and C_p the specific heat of the solid in ergs per gram. The numerical values of the constants used in the calculation of this correction term have been taken from the *Landolt-Bornstein Tables* and the *International Critical Tables.*

The compressibility determinations made in Bridgman's laboratory usually extended upto very high pressures. We naturally make use of the compressibility value for zero pressures computed by the investigators

themselves from the experimental data. The values reported by Bridgman and Slater prior to 1946 are subject to correction by a constant term $-0{\cdot}033\times10^{-7}\ kg^{-1}\cdot cm.^2$ in the light of Bridgman's latest determination of the linear compressibility of iron. Since the compressibility as well as the other elastic constants are functions of temperature, it is necessary that the comparison should be made for their values at the same temperature, either as reported by the authors themselves or as reduced to the same temperature from a knowledge of the variation of the elastic constants with temperature.

In selecting the substances the data for which are discussed in the present paper, the choice has naturally fallen on those substances which have been frequently the subject of experimental study. It so happens that these substances also fall into well-defined groups being very similar in chemical composition and their crystal structure, *e.g.*, NaCl, KCl, KBr, NaBr, LiF, MgO and AgCl, all of which have the rock-salt structure; diamond, silicon, germanium, zinc blende and fluorspar all of which again have closely similar structures and finally the metallic elements aluminium, copper, nickel and silver which have the face-centred cubic structure. In tabulating our final results we have arranged the substances in the order stated, in order to facilitate intercomposition of their elastic behaviour.

3. CRYSTALS WITH THE ROCK-SALT STRUCTURE

(*a*) *Rock-salt.*—The elastic constants of NaCl were determined by Voigt first in 1888 by the methods of torsion and flexure. Bridgman has also in 1929 determined the constants by the same methods. With the development of techniques based on ultrasonic wave-propagation, several determinations have been made recently by numerous investigators namely, Bergmann, Rose, Durand, Hunter and Siegel, Huntington, Galt, Lazarus and Bhagavantam. The values reported by these investigators and the methods used by them are given in Table I.

The values for C_{12} reported by the investigators who have used the static methods are distinctly higher than the values for the same constant obtained using dynamic methods, and this difference appears to be larger than can be reasonably ascribed to experimental errors. On the other hand, the values for C_{11} and C_{44} do not exhibit such a difference. The close agreement between the results reported by the three investigators who have used the pulse technique indicate that this method yields precise results. Hence, the mean of the values reported by these three workers have been adopted here as the best values.

TABLE I

Author	Method	C_{11}	C_{12}	C_{44}
Voigt ..	Static	4·77	1·32	1·29
Bridgman ..	,,	4·94	1·37	1·28
Bergmann ..	Diffraction patterns	4·77	1·25	1·21
Rose (270° K.) ..	Composite oscillator	5·06	1·30	1·278
Durand (300° K.) ..	,,	4·96	1·31	1·268
Hunter and Siegel ..	,,	4·86	1·194	1·281
Huntington (25° C.) ..	Pulse	4·85	1·23	1·265
Galt (298° K.) ..	,,	4·87	1·24	1·260
Lazarus (298° K.) ..	,,	4·911	1·225	1·284
Bhagavantam (R. T.) ..	Ultrasonic	4·97	1·27	1·27

The isothermal compressibility had been determined by static methods by a series of investigators, *viz.*, Rontgen and Schneider, Madelung and Fuchs, Richards and Jones, Adams, Williamson and Johnston, Slater and Bridgman. Table II shows the values reported by the various authors. Of these, the

TABLE II

Author	Temp.	χ in 10^{-7} kg.$^{-1}$ cm.^{2}
Rontgen and Schneider	R.T.	50
Madelung and Fuchs ..	0° C.	40·5
Richards and Jones ..	20° C.	44·0
Adams, Williamson and Johnston	R.T.	40·4
Slater ..	30° C.	41·8
Bridgman ..	30° C.	41·82
	75° C.	43·44

most accurate are evidently those reported by Slater and Bridgman, and they have accordingly been adopted as correct. The values reported by Madelung and Fuchs refer to the pressure range 50–200 kg./cm.^{2}, those of Richards and Jones to the range 100–510 kg./cm.^{2} The values of Slater and Bridgman quoted are for zero-pressure always.

These values are however subject to correction by a constant term $-0{\cdot}033 \times 10^{-7}$ kg.$^{-1}$ cm.^{2} in the light of Bridgman's latest determination of the linear compressibility of iron. After making this correction and using the known value of g at Harvard, the isothermal compressibility of rock-salt comes out as $42{\cdot}62 \times 10^{-13}$ cm.^{2}/dyne at 30° C. The value of the compressibility at 25° C. is found by linear interpolation from the values reported by him at 30° C. and 75° C. This correction when effected leads to a value of χ (isothermal) $= 42{\cdot}44$. The difference between the isothermal and adiabatic compressibilities can be calculated from the formula given earlier. For rock-salt, the numerical values used in the formula are: $\alpha = 44 \times 10^{-6}$; $\rho = 2{\cdot}168$; $C_p = 0{\cdot}2078$ cal./gm. The value of the adiabatic compressibility at 25° C. is found to be $39{\cdot}68 \times 10^{-13}$ cm.^{2}/dyne. Hence the bulk modulus comes out as $2{\cdot}52 \times 10^{11}$ dynes/cm.^{2} On the other hand, the value for the bulk modulus calculated from the formula $(C_{11} + 2C_{12})/3$ comes out as $2{\cdot}45 \times 10^{11}$ dynes/cm.^{2} the difference clearly being greater than can be explained in terms of experimental errors. The average values of the dynamically determined constants used in the calculation are: $C_{11} = 4{\cdot}877$; $C_{12} = 1{\cdot}232$; $C_{44} = 1{\cdot}269 \times 10^{11}$ dynes/cm.^{2}, while the four constants evaluated in the manner already explained come out as $d_{11} = 4{\cdot}88$; $d_{12} = 1{\cdot}34$; $d_{44} = 1{\cdot}27$; and $d_{45} = 1{\cdot}16 \times 10^{11}$ dynes/cm.^{2}

(*b*) *Potassium Chloride.*—The elastic constants of KCl have been determined by static methods by Voigt, Forsterling and Bridgman. The later workers who have determined the elastic constants by the dynamic methods of ultrasonics are Durand, Galt and recently Lazarus. Their values appear in Table III.

It will be noticed from Table III that the values reported by the different authors are in much less satisfactory agreement amongst themselves than in the case of rock-salt. The values for C_{12} in particular appear rather erratic and this is probably due to the fact that measurements usually involve the determination of linear combinations of C_{11} and C_{12} and since C_{12} is much smaller of the two, errors of measurement would influence its determined value very noticeably. Voigt gives C_{12} to three significant figures but his value is undoubtably an error. As in the case of rock-salt we shall

TABLE III

Author		Method	C_{11}	C_{12}	C_{44}
Voigt	R.T. ..	Static	3·75	0·198	0·655
Forsterling	R.T. ..	,,	3·88	0·640	0·65
Bridgman	30° C. ..	,,	3·70	0·81	0·79
Durand	R.T. ..	Composite oscillator	4·00	0·6	0·625
Galt	25° C. ..	Pulse	3·98	0·625	0·62
Lazarus	25° C. ..	,,	4·095	0·705	0·630

assume as a definitive value the mean of the measurements by the pulse method at 25° C.

The static measurements of compressibilities by different authors shown in Table IV agree remarkably well amongst themselves. We shall here accept the measurement by Slater as corrected by Bridgman to be the most

TABLE IV

Author	Temp.	χ in 10^{-7} kg.$^{-1}$ cm.^{2}
Rontgen and Schneider ..	..	56
Madelung and Fuchs ..	0° C.	55·1
Richards and Jones ..	20° C.	53·0
Slater ..	30° C.	55·2

reliable. This comes out as $56{\cdot}27\times10^{-13}$ dynes^{-1} cm.^{2} at 30° C. and after correction using the temperature coefficient given by Slater, the value at 25° C. is found as $56{\cdot}14\times10^{-13}$ cm.^{2}/dyne. From this the adiabatic compressibility at 25° C. is calculated using the following values for KCl in the correction formula.

$\alpha = 36\times10^{-6}$; $\rho = 1{\cdot}992$; and $C_p = 0{\cdot}1661$ cal./gm. The adiabatic compressibility is found to have a value $53{\cdot}62\times10^{-13}$. Hence the bulk modulus at 25° C. comes out as $1{\cdot}865\times10^{11}$ dynes/cm.^{2}

The mean values for C_{11}, C_{12} and C_{44} adopted are 4·038, 0·663 and $0{\cdot}628\times10^{11}$ respectively. The bulk-modulus calculated using the classical expression $(C_{11}+2C_{12})/3$ comes out as $1{\cdot}788\times10^{11}$ dynes/cm.^{2}, which is definitely smaller than the experimentally determined value. The values found for the four elastic constants of the new theory are respectively: $d_{11}=4{\cdot}038$; $d_{12}=0{\cdot}779$; $d_{44}=0{\cdot}628$; $d_{45}=0{\cdot}512\times10^{11}$ dynes/cm.^{2}

(*c*) *Potassium Bromide.*—Static measurements of the elastic constants have been reported by Bridgman. Using the pulse technique Huntington and Galt have independently determined the constants at room temperature. The values are given in Table V.

TABLE V

Author		Method	C_{11}	C_{12}	C_{44}
			$\times10^{11}$ dynes/cm.^{2}		
Bridgman	30° C. . .	Static	3·33	0·58	0·62
Huntington	25° C. . .	Pulse	3·45	0·54	0·508
Galt	25° C. . .	,,	3·46	0·58	0·505

The compressibility measurements have been made by Richards and Jones, and Slater independently and the values reported are $6{\cdot}5\times10^{-6}$kg.$^{-1}$cm.^{2} at 20° C. and $6{\cdot}57\times10^{-6}$ kg.$^{-1}$ cm.^{2} at 30° C. respectively, being in good agreement with each other. Using the temperature coefficient given by Slater, the isothermal compressibility at 25° C. on calculation is found to be $66{\cdot}78\times10^{-13}$ cm.^{2} dyne^{-1}. The adiabatic compressibility is found using the correction formula given earlier. The values adopted for KBr are: $\alpha=41\times10^{-6}$; $\rho=2{\cdot}756$; $C_p=0{\cdot}1033$ cal./gm. $\chi_{(\text{adiabatic})}$ comes out as $62{\cdot}99\times10^{-13}$ cm.^{2}/dyne and hence the bulk modulus is $1{\cdot}588\times10^{11}$ dynes/cm.^{2} at 25° C.

Adopting the mean of the values given by Galt and Huntington the bulk modulus in terms of the classical formula $(C_{11}+2C_{12})/3$ is found to be $1{\cdot}525\times10^{11}$ dynes/cm.^{2}, thus differing from the actually observed value corrected for the adiabatic nature of deformation.

The values adopted for the elastic constants are $C_{11}=3{\cdot}455$, $C_{12}=0{\cdot}56$, $C_{44}=0{\cdot}507$, while the four constants evaluated in the manner explained are $d_{11}=3{\cdot}455$; $d_{12}=0{\cdot}655$; $d_{44}=0{\cdot}507$; $d_{45}=0{\cdot}412\times10^{11}$ dynes/cm.^{2}

(*d*) *Sodium Bromide.*—The static measurements of the elastic constants are due to Bridgman, while they have been determined by Bhagavantam using ultrasonic methods.

TABLE VI

Author	Temp.	C_{11}	C_{12}	C_{44}
Bridgman ..	30° C.	3·30	1·31	1·33
Bhagavantam ..	R.T.	3·87	0·97	0·97

The values reported by Bhagavantam differ appreciably from those of Bridgman. However, we shall take for our calculations the values determined by dynamic methods as usual, since the identification of the constants of the new theory with that of the older theory is by identifying the two wave-equations.

The compressibility determinations in the case of NaBr have been made by Richards and Saerens at 20° C., the value being $5{\cdot}4\times10^{-6}$ kg.$^{-1}$ cm.^{2} in the pressure range 100–510 kg/cm.^{2}, and by Slater at 30° C. who reports a zero pressure value of $4{\cdot}98\times10^{-6}$ kg.$^{-1}$ cm.^{2} The isothermal compressibility at 30° C. is found to be $50{\cdot}762\times10^{-13}$ cm.^{2}/dyne. Correcting this to the adiabatic value we get $\chi_{(\text{adiabatic})}$ as 47·576. The values used in the calculation of the correction term are: $\alpha = 43\times10^{-6}$; $\rho = 3{\cdot}213$; $C_p = 0{\cdot}1178$ cal./gm. The bulk modulus value hence comes out as $2{\cdot}102\times10^{11}$ dynes/cm.^{2} whereas according to the classical theory this value should be $1{\cdot}936\times10^{11}$ dynes/cm.^{2}

The values of the elastic constants according to the new theory are: $d_{11} = 3{\cdot}87$; $d_{12} = 1{\cdot}22$; $d_{44} = 0{\cdot}97$; $d_{45} = 0{\cdot}72\times10^{11}$ dynes/cm.^{2}

(*e*) *Lithium Fluoride.*—The elastic constants of LiF have been determined by dynamic methods by Bergmann, Huntington, Sundara Rao and Seshagiri Rao and their values are shown in Table VII.

It will be noticed that there are notable divergences between the values reported by different investigators though they all use ultrasonic methods. A clue to the origin of these differences is to be found in the differences in density reported by the different investigators in their respective papers. The density of LiF calculated from the lattice spacing and known atomic weights is 2·627, while Huntington, Seshagiri Rao and Sundara Rao give the density as 2·295, 2·635 and 2·601 respectively. The value found in Landolt Bornstein Table is 2·640. As the value reported by Seshagiri Rao corresponds to this, we use his data in our calculations.

TABLE VII

Author		Method	C_{11}	C_{12}	C_{44}
Bergman	R.T. ..	Diffraction patterns	12·0	4·41	6·4
Huntington	25° C. ..	Pulse	9·74	4·04	5·54
Sundara Rao	R.T. ..	Ultrasonic	11·9	4·58	5·42
Seshagiri Rao	R.T. ..	,,	11·9	5·38	5·34

The compressibility of LiF has been determined by Slater as $15{\cdot}3 \times 10^{-7}$ kg.$^{-1}$ cm.^{2} at 30° C. and in a redetermination Bridgman has corrected this value and gives it as $14{\cdot}95 \times 10^{-7}$ kg.$^{-1}$ cm.^{2} The isothermal compressibility at 30° C. is accordingly $15{\cdot}215 \times 10^{-13}$ cm.^{2} dyne^{-1}. The following values are used in the correction term for adiabatic compressibility: $\alpha = 36 \times 10^{-6}$; $\rho = 2{\cdot}64$; and $C_p = 0{\cdot}373$ cal./gm. The adiabatic compressibility comes out as $14{\cdot}357 \times 10^{-13}$ and hence the bulk modulus as $6{\cdot}965 \times 10^{11}$ dynes/cm.^{2}, while the bulk modulus using the data of Seshagiri Rao and the classical formula $(C_{11} + 2C_{12})/3$ is found to be having a different value of $7{\cdot}55 \times 10^{11}$ dynes/cm.^{2} Using the values of Seshagiri Rao in our calculation we find the following values for the four elastic constants. $d_{11} = 11{\cdot}9$; $d_{12} = 4{\cdot}5$; $d_{44} = 5{\cdot}34$; and $d_{45} = 6{\cdot}22 \times 10^{11}$ dynes/cm.^{2}

(*f*) *Magnesium Oxide.*—The elastic constants of MgO have been determined dynamically by Durand and by Bhagavantam and their values are shown below:—

TABLE VIII

Author		C_{11}	C_{12}	C_{44}
Durand	30° C. ..	28·92	8·77	15·47
Bhagavantam	R.T. ..	28·6	8·7	14·8

Their values agree fairly well and the slight difference in the value of C_{44} might be due to experimental errors. No static determinations of the elastic constants appear to have been made.

The compressibility of MgO has been determined by Madelung and Fuchs and by Bridgman. The former investigators report varying values

with the different specimens they used, while Bridgman using a clear single crystal has reported the value of $5{\cdot}904\times10^{-7}$ kg.$^{-1}$ cm.^{2} at 30° C. The isothermal compressibility at 30° C. is hence $5{\cdot}988\times10^{-13}$ cm.^{2}/dyne. The values of the constants appearing in the correction term are: $\alpha = 13{\cdot}3\times10^{-6}$; $\rho = 3{\cdot}576$; $C_p = 0{\cdot}2297$ cal./gm. The adiabatic compressibility comes out as $5{\cdot}847\times10^{-13}$ and hence the bulk modulus as $17{\cdot}10\times10^{11}$ dynes/cm.^{2}

We shall make use of the mean of the two dynamic determinations for the purposes of our calculation, *i.e.*, $C_{11} = 28{\cdot}76$; $C_{12} = 8{\cdot}74$ and $C_{44} = 15{\cdot}14$. The compressibility calculated using the formula $(C_{11} + 2C_{12})/3$ is found to be equal to $15{\cdot}41\times10^{11}$ dynes/cm.^{2}, being distinctly different from the observed and corrected value of $17{\cdot}10\times10^{11}$. The elastic constants according to the new theory are as follows: $d_{11} = 28{\cdot}76$; $d_{12} = 11{\cdot}27$; $d_{44} = 15{\cdot}14$; $d_{45} = 12{\cdot}61\times10^{11}$ dynes/cm.^{2}

(*g*) *Silver Chloride.*—The elastic constants of AgCl have been recently determined using the pulse method by Arenberg (1950). The values have been reported for two different specimens and show good agreement between themselves. However, it is stated by him that the values from one of the specimens are to be preferred and they are given as $C_{11} = 6{\cdot}05$; $C_{12} = 3{\cdot}64$. $C_{44} = 0{\cdot}624\times10^{11}$ dynes/cm.^{2} The compressibility of fused and solidified AgCl has been determined by Richards and Jones, while Bridgman has studied the case of AgCl with compressed powder. The isothermal bulk-modulus value of $4{\cdot}12\times10^{11}$ obtained by extrapolating Bridgman's data to zero pressure agrees well with the value of $4{\cdot}17\times10^{11}$ dynes/cm.^{2} reported by Richards and Jones. Adopting the value due to Bridgman and using the values $\alpha = 30\times10^{-6}$; $\rho = 5{\cdot}5$; and $C_p = 0{\cdot}0875$ cal./gm. for AgCl, the adiabatic bulk modulus is found to be $4{\cdot}338\times10^{11}$ dynes/cm.^{2} According to the classical formula $(C_{11} + 2C_{12})/3$ this value comes out as $4{\cdot}444\times10^{11}$ dynes/cm.^{2}, being different from the value given above. The four elastic constants according to the new theory are: $d_{11} = 6{\cdot}05$; $d_{12} = 3{\cdot}482$; $d_{44} = 0{\cdot}624$; $d_{45} = 0{\cdot}782\times10^{11}$ dynes/cm.^{2}

4. Crystals with the Diamond-like Structure

(*a*) *Diamond.*—The elastic constants of diamond have been determined by the ultrasonic wedge method by Bhagavantam and Bhimasenachar (1946). The following are the values reported by them. $C_{11} = 9{\cdot}5\times10^{12}$; $C_{12} = 3{\cdot}9\times10^{12}$ and $C_{44} = 4{\cdot}3\times10^{12}$ dynes/cm.^{2} The compressibility has been determined first by Adams and again by Williamson in the same laboratory, the values being $0{\cdot}16\times10^{-12}$ and $0{\cdot}18\times10^{-12}$ cm.^{2}/dyne respectively.

The latter value is reported to be preferred since better material was used in the determination by Williamson. This gives a value of $5{\cdot}56\times10^{12}$ dynes/cm.^{2} for the isothermal bulk modulus. The correction for the adiabatic bulk modulus is negligible. Using this value of $5{\cdot}56\times10^{12}$ and the reported values for the elastic constants the values of the four elastic constants are calculated. They are: $d_{11}=9{\cdot}5$; $d_{12}=3{\cdot}59$; $d_{44}=4{\cdot}30$; and $d_{45}=4{\cdot}61\times10^{12}$ dynes/cm.^{2}

(*b*) *Germanium.*—The elastic constants of Ge have been determined by ultrasonic methods by Bond and others, Fine and McSkimin and their values are shown in Table IX.

TABLE IX

Author	Method	C_{11}	C_{12}	C_{44}
Bond and others 25° C. ..	Pulse	12·90	4·84	6·69
Fine 25° C. ..	Composite Oscillator	13·16	5·09	6·69
McSkimin 30° C. ..	Pulse	12·88	4·825	6·705

All the determinations have been made in the Bell Telephone Laboratories and McSkimin and Fine have studied the variations of the constants with temperature. The values show good agreement between themselves. The values due to McSkimin are taken from the graphs given by him exhibiting the variation of the elastic constants with temperature.

The compressibility of *polycrystalline* germanium has been determined by Bridgman at 30° C. on two occasions with different specimens and the values are $13{\cdot}78\times10^{-7}$ kg.$^{-1}$ cm.^{2} and $14{\cdot}11\times10^{-7}$ kg.$^{-1}$ cm.^{2} and the latter value is said to be more reliable. The isothermal compressibility at 30° C. is hence $14{\cdot}358\times10^{-13}$ cm.^{2}/dyne. The constants used in the correction term to find the adiabatic compressibility are: $\alpha=5{\cdot}5\times10^{-6}$; $\rho=5{\cdot}323$; $C_p=22{\cdot}3$ Joules/gm. atom. The corrected value of the adiabatic compressibility is $14{\cdot}308\times10^{-13}$ cm.^{2}/dyne and hence the bulk modulus value is $6{\cdot}989\times10^{11}$ dynes/cm.^{2}

The elastic constants for 30° C. could be more accurately and directly obtained from McSkimin's detailed data. Using his values we find that the bulk modulus value according to the classical formula should be $7{\cdot}51\times10^{11}$ dynes/cm.^{2} The four elastic constants are found to be $d_{11}=12{\cdot}88$; $d_{12}=4{\cdot}04$; $d_{44}=6{\cdot}705$; and $d_{45}=7{\cdot}49\times10^{11}$ dynes/cm.^{2}

(*c*) *Silicon.*—The elastic constants of crystalline silicon have been determined by McSkimin and others and subsequently in detail by McSkimin over a wide range of temperatures. The following values for the constants at 30° C. are found from the graphs given by him. $C_{11} = 16{\cdot}56$; $C_{12} = 6{\cdot}386$; $C_{44} = 7{\cdot}953 \times 10^{11}$ dynes/cm.^{2} The compressibility of *polycrystalline* silicon has been determined over a wide range of pressures by Bridgman at 30° C. and on extrapolating his values to zero pressure, the isothermal compressibility is found to be $9{\cdot}92 \times 10^{-7}$ kg.$^{-1}$ cm.^{2}, *i.e.*, $10{\cdot}118 \times 10^{-13}$ dynes^{-1} cm.^{2} The following values are used in the correction term for adiabatic compressibility. $\alpha = 2{\cdot}25 \times 10^{-6}$; $\rho = 2{\cdot}331$; $C_p = 0{\cdot}1712$ cal./gm. On correction the adiabatic compressibility is found to be $10{\cdot}11 \times 10^{-13}$ dynes^{-1} cm.^{2} and hence the bulk modulus as $9{\cdot}89 \times 10^{11}$ dynes/cm.^{2} The value calculated using the formula $(C_{11} + 2C_{12})/3$ is found to be $9{\cdot}78 \times 10^{11}$ dynes/cm.^{2} The four elastic constants calculated are: $d_{11} = 16{\cdot}56$; $d_{12} = 6{\cdot}56$; $d_{44} = 7{\cdot}953$; and $d_{45} = 7{\cdot}78 \times 10^{11}$ dynes/cm.^{2}

(*d*) *Zinc blende.*—The elastic constants of zinc blende have been reported by Bhagavantam and Suryanarayana using ultrasonic methods. The constant C_{44} has however been obtained by them from static torsion experiments. The crystalline material used by them contained only 94% of zinc sulphide. The following values are reported by them. $C_{11} = 10{\cdot}79 \times 10^{11}$; $C_{12} = 7{\cdot}22 \times 10^{11}$; $C_{44} = 4{\cdot}12 \times 10^{11}$. These values are in disagreement with the values reported by Voigt from static methods, which are: $C_{11} = 9{\cdot}43 \times 10^{11}$; $C_{12} = 5{\cdot}68 \times 10^{11}$; $C_{44} = 4{\cdot}37 \times 10^{11}$.

The compressibility of a single crystal of zinc blende has been determined by Bridgman as $12{\cdot}81 \times 10^{-7}$ kg.$^{-1}$ cm.^{2} at 30° C. This gives a value of $13{\cdot}032 \times 10^{-13}$ dynes^{-1} cm.^{2} at 30° C. for the isothermal compressibility. The constants used in the correction term for adiabatic compressibility are: $\alpha = 6{\cdot}7 \times 10^{-6}$; $\rho = 4{\cdot}102$; and $C_p = 0{\cdot}1146$ cal./gm. The corrected value of the adiabatic compressibility is found to be $12{\cdot}97 \times 10^{-13}$ dynes^{-1} cm.^{2}, and hence the bulk modulus is $7{\cdot}71 \times 10^{11}$ dynes/cm.^{2} The bulk-modulus calculated from the formula $(C_{11} + 2C_{12})/3$ using Bhagavantam and Suryanarayana's values is $8{\cdot}41 \times 10^{11}$ whereas Voigt's values give $6{\cdot}93 \times 10^{11}$ dynes/cm.^{2}

In the calculation of the four elastic constants, we make use of Bhagavantam and Suryanarayana's values since they are for the major part obtained from dynamic methods. We obtain the following values for the constants. $d_{11} = 10{\cdot}79$; $d_{12} = 6{\cdot}17$; $d_{44} = 4{\cdot}12$; and $d_{45} = 5{\cdot}17 \times 10^{11}$ dynes/cm.^{2}

(*e*) *Fluorspar.*—The elastic constants of fluorspar have been determined using static methods by Voigt, and by Bergmann and Bhagavantam using dynamic methods. Their values are shown in Table X.

TABLE X

Author	Method	C_{11}	C_{12}	C_{44}
Voigt ..	Static	16·4	4·47	3·38
Bergmann ..	Diffraction patterns	16·76	4·72	3·69
Bhagavantam ..	Ultrasonic	16·44	5·02	3·47

For our calculations we take here the mean of the values of Bergmann and Bhagavantam, *i.e.*, $C_{11} = 16{\cdot}6$; $C_{12} = 4{\cdot}87$; and $C_{44} = 3{\cdot}58 \times 10^{11}$ dynes/cm.^{2}

The compressibility of CaF_2 has been determined by Madelung and Fuchs at 0° C. and in the pressure range 50–200 kg./cm.^{2} and the value reported by them is $12{\cdot}2 \times 10^{-7}$ kg.$^{-1}$ cm.^{2} Bridgman has also determined the compressibility at 30° C. and reports a zero pressure value of $12{\cdot}06 \times 10^{-7}$ kg.$^{-1}$ cm.^{2}, *i.e.*, $12{\cdot}267 \times 10^{-13}$ cm.^{2}/dyne. The values used in the correction term are: $\alpha = 19{\cdot}11 \times 10^{-6}$; $\rho = 3{\cdot}18$; $C_p = 0{\cdot}887$ Joules/gm. The adiabatic compressibility value is found to be $11{\cdot}914 \times 10^{-13}$ cm.^{2}/dyne and hence the bulk modulus is $8{\cdot}39 \times 10^{11}$ dynes/cm.^{2} The bulk modulus value using the formula $(C_{11} + 2C_{12})/3$ is found to be $8{\cdot}78 \times 10^{11}$ dynes/cm.^{2}

The four elastic constants calculated are: $d_{11} = 16{\cdot}6$; $d_{12} = 4{\cdot}29$; $d_{44} = 3{\cdot}58$; and $d_{45} = 4{\cdot}16 \times 10^{11}$ dynes/cm.^{2}

5. METALS CRYSTALLIZING IN THE CUBIC SYSTEM

(*a*) *Aluminium.*—The elastic constants of single crystals of aluminium have been determined using static methods by Goens. Recently Lazarus and Sutton have independently measured the elastic constants by ultrasonic methods. The values reported by all these investigators are shown in Table XI.

The accuracy in the measurements of Lazarus is greater than that of Sutton as is evidenced by the comments made by them in their respective papers. Moreover the purity of the specimens used by Lazarus and Sutton is given as 99·99% and 99·93% respectively. In view of these facts we take Lazarus's values for the purposes of our calculation.

TABLE XI

Author	Method	C_{11}	C_{12}	C_{44}
Goens R.T. ..	Static	10·82	6·22	2·84
Lazarus 25° C. ..	Pulse	10·56	6·39	2·853
Sutton 20° C. ..	Composite oscillator	11·29	6·65	2·783

The isothermal compressibility of aluminium single crystals has been determined by Bridgman as $13{\cdot}38\times10^{-7}$ kg.$^{-1}$ cm.^{2} at 30° C. and as $13{\cdot}76\times10^{-7}$ kg.$^{-1}$ cm.^{2} at 75° C. The value at 25° C. on linear extrapolation comes out as $13{\cdot}338\times10^{-7}$ kg.$^{-1}$ cm.^{2}, *i.e.*, $13{\cdot}57\times10^{-13}$ dynes^{-1} cm.^{2} The following values for the constants are used in the correction term for adiabatic compressibility: $\alpha = 23{\cdot}06\times10^{-6}$; $\rho = 2{\cdot}702$; $C_p = 0{\cdot}2129$ cal./gm. The adiabatic compressibility is found to be $12{\cdot}97\times10^{-13}$ dynes^{-1} cm.^{2} and hence the bulk modulus is $7{\cdot}71\times10^{11}$ dynes/cm.^{2} The bulk modulus obtained from the values of Lazarus is $7{\cdot}78\times10^{11}$. The values of the four elastic constants calculated are: $d_{11} = 10{\cdot}56$; $d_{12} = 6{\cdot}29$; $d_{44} = 2{\cdot}853$; $d_{45} = 2{\cdot}953\times10^{11}$ dynes/cm.^{2}

(*b*) *Copper.*—The elastic constants of copper single crystals have been determined using the composite oscillator method by Goens and Weerts. Recently Lazarus, Long, and Overton and Gaffney have determined the constants using pulse methods. The values are shown in Table XII.

TABLE XII

Author	Method	C_{11}	C_{12}	C_{44}
Goens and Weerts R.T. ..	Composite oscillator	16·98	12·26	7·53
Lazarus 25° C. ..	Pulse	17·1	12·39	7·56
Long 300° K. ..	,,	16·83	12·21	7·54
Overton and Gaffney 300° K. ..	,,	16·84	12·14	7·54

There is very good agreement between the three sets of values determined by the pulse method and hence for the purposes of our calculation we shall make use of the mean of these values.

The compressibility of polycrystalline copper of high purity has been determined by Bridgman as $7\cdot19\times10^{-7}$ kg.$^{-1}$ cm.^{2} at 30° C. and $7\cdot34\times10^{-7}$ at 75° C. Hence the value at 300° K. is found to be $7\cdot173\times10^{-7}$ kg.$^{-1}$ cm.^{2}, *i.e.*, $7\cdot283\times10^{-13}$ dynes^{-1} cm.^{2} The following values are used in the correction term for the adiabatic compressibility: $\alpha = 17\cdot09\times10^{-6}$; $\rho = 8\cdot92$; $C_p = 0\cdot0919$ cal./gm. The corrected value of adiabatic compressibility is $7\cdot05\times10^{-13}$ dynes^{-1} cm.^{2} and hence the bulk modulus is $14\cdot18\times10^{11}$ dynes/cm.^{2} The average values of the elastic constants from pulse method are: $C_{11} = 16\cdot92$; $C_{12} = 12\cdot25$; and $C_{44} = 7\cdot55\times10^{11}$ dynes/cm.^{2} The bulk modulus using the formula $(C_{11} + 2C_{12})/3$ is found to be $13\cdot81\times10^{11}$ dynes/cm.^{2} The four elastic constants calculated are: $d_{11} = 16\cdot92$; $d_{12} = 12\cdot81$; $d_{44} = 7\cdot55$; and $d_{45} = 6\cdot99\times10^{11}$ dynes/cm.^{2}

(*c*) *Nickel.*—The elastic constants of single crystals of nickel have been determined recently using the ultrasonic pulse method by Bozorth and others and also by Neighbours and others. Their values are given in Table XIII.

TABLE XIII

Author	C_{11}	C_{12}	C_{44}
	in 10^{12} dynes/cm.^{2}		
Bozorth and others ..	2·53	1·58	1·22
,, ..	2·524	1·538	1·23
,, ..	2·523	1·566	1·23
Neighbours and others ..	2·528	1·52	1·238

The average value of these at 25° C. are: $C_{11} = 2\cdot526$; $C_{12} = 1\cdot551$; and $C_{44} = 1\cdot23\times10^{12}$ dynes/cm.^{2}

The compressibility of pure nickel has been determined by Bridgman at 30° C. as $5\cdot29\times10^{-7}$ kg.$^{-1}$ cm.^{2} and at 75° C. as $5\cdot35\times10^{-7}$. The value at 25° C. is hence $5\cdot283\times10^{-7}$ kg.$^{-1}$ cm.^{2} The isothermal compressibility is hence $5\cdot355\times10^{-13}$ dynes^{-1} cm.^{2} The values used in the correction term for adiabatic compressibility are: $\alpha = 13\cdot15\times10^{-6}$; $\rho = 8\cdot9$; and $C_p = 0\cdot107$ cal./gm. The adiabatic compressibility is found to be $5\cdot239\times10^{-13}$ dynes^{-1} cm.^{2} and hence the bulk modulus is $19\cdot09\times10^{11}$ dynes/cm.^{2} The bulk modulus using the classical formula is found to be $18\cdot76\times10^{11}$ dynes/cm.^{2} The four elastic constants calculated are: $d_{11} = 25\cdot26$; $d_{12} = 16\cdot01$; $d_{44} = 12\cdot3$; and $d_{45} = 11\cdot8\times10^{11}$ dynes/cm.^{2}

(*d*) *Silver.*—The elastic constants of single crystals of silver have been determined by Rohl using the classical static and dynamic methods. The constants have been recently determined by Bacon and Smith using the ultrasonic pulse method. The values are shown below:—

TABLE XIV

Author	Method	C_{11}	C_{12}	C_{44}
Rohl R.T. ..	Static, etc.	11·9	8·94	4·37
Bacon and Smith R.T. ..	Pulse	12·4	9·34	4·61

The compressibility of pure silver has been determined by Bridgman at 30° C. as $9{\cdot}87\times10^{-7}$ kg.$^{-1}$ cm.^{2}, *i.e.*, $10{\cdot}034\times10^{-13}$ dynes^{-1} cm.^{2} The constants used in the correction term are: $\alpha = 18{\cdot}9\times10^{-6}$; $\rho = 10{\cdot}5$; $C_p = 25{\cdot}2$ Joules/gm. atom. The adiabatic compressibility is found to be $9{\cdot}939\times10^{-13}$ dynes^{-1} cm.^{2} and hence the bulk modulus is $10{\cdot}06\times10^{11}$ dynes/cm.^{2} The value calculated using the formula $(C_{11} + 2C_{12})/3$ is found to be $10{\cdot}36\times10^{11}$ dynes/cm.^{2} The four constants calculated are: $d_{11} = 12{\cdot}4$; $d_{12} = 8{\cdot}89$; $d_{44} = 4{\cdot}61$; and $d_{45} = 5{\cdot}06\times10^{11}$ dynes/cm.^{2}

6. SOME FINAL REMARKS

In Table XV the results for the individual cases given in the foregoing pages have been collected together. The columns C_{11}, C_{12} and C_{44} show the results of the ultrasonic measurements, while the columns d_{11}, d_{12}, d_{44} and d_{45} represents the constants as evaluated from the ultrasonic data in conjunction with the bulk modulus as determined by Bridgman and his collaborators after making *all* necessary corrections. The values of C_{11} and d_{11} are in each case identical; likewise those of C_{44} and d_{44}. But C_{12} and d_{12} are different and such difference is a measure of the failure of the three constant-theory to represent the actual elastic behaviour of the crystal. The difference between d_{44} and d_{45} also expresses the same situation in another way.

Certain general features emerge from the table. For all the four alkali halides which are soluble in water, C_{12} is less than d_{12} and likewise d_{45} is less than d_{44}. This regularity of behaviour taken in conjunction with the reliability of the data in these cases makes it clear that these differences are real and justify us in concluding that the elastic behaviour of cubic crystals cannot be expressed in terms of three constants, but needs four. Diamond,

germanium, zinc blende and fluorspar also exhibit a parallel behaviour which is the reverse of that shown by the four water-soluble alkali halides. In their cases, C_{12} is decidedly greater than d_{12}, while *per contra* d_{44} is less than d_{45} and these differences are numerically more striking than in the case of the alkali halides. Magnesium oxide for which the data are reliable exhibits

TABLE XV

Elastic Constants in 10^{11} *dynes/cm.*^{2}

Substance	C_{11}	C_{12}	C_{44}	d_{11}	d_{12}	d_{44}	d_{45}
NaCl ..	4·877	1·232	1·269	4·877	1·34	1·269	1·16
KCl ..	4·038	0·663	0·628	4·038	0·779	0·628	0·512
KBr ..	3·455	0·56	0·507	3·455	0·655	0·507	0·412
NaBr ..	3·87	0·97	0·97	3·87	1·22	0·97	0·72
LiF ..	11·9	5·38	5·34	11·9	4·5	5·34	6·22
MgO ..	28·76	8·74	15·14	28·76	11·27	15·14	12·61
AgCl ..	6·05	3·64	0·624	6·05	3·482	0·624	0·782
Diamond ..	95	39	43	95	35·9	43·0	46·1
Ge ..	12·88	4·825	6·705	12·88	4·04	6·705	7·49
Si ..	16·56	6·386	7·953	16·56	6·56	7·953	7·78
ZnS ..	10·79	7·22	4·12	10·79	6·17	4·12	5·17
CaF_2 ..	16·6	4·87	3·58	16·6	4·29	3·58	4·16
Al ..	10·56	6·39	2·853	10·56	6·29	2·853	2·953
Cu ..	16·92	12·25	7·55	16·92	12·81	7·55	6·99
Ni ..	25·26	15·51	12·3	25·26	16·01	12·3	11·8
Ag ..	12·4	9·34	4·61	12·4	8·89	4·61	5·06

a noteworthy behaviour; the differences between C_{12} and d_{12} and likewise between d_{44} and d_{45} are in the same sense as in the alkali halides but proportionately much larger. Differences of the same order of magnitude but in the opposite sense are shown by lithium fluoride. In the case of the metals crystallising in the face-centred cubic system, we also find differences between C_{12} and d_{12} and between d_{44} and d_{45}, but they are not always in the same sense. This is a feature which need not surpirse us in view of the very great differences exhibited by these metals in other respects.

7. SUMMARY

The belief that the elastic behaviour of cubic crystals can be described in terms of three constants rests on theoretical considerations which are examined in the paper and shown to be indefensible. The correct theory demands four constants for cubic crystals belonging to the O_h and T_d classes.

The experimental results for sixteen different crystals belonging to these classes for which the most precise data are available are critically examined and it is shown that the adiabatic bulk modulus as computed respectively from the observed velocities of ultrasonic wave propagation and from the static determinations of compressibility made at Harvard are in systematic disagreement. The data show very clearly that the elastic behaviour of these crystals cannot be expressed in terms of three constants, but needs four. The latter have been computed and tabulated.

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ON HAUSDORFF TRANSFORMATIONS FOR DOUBLE SEQUENCES

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Introduction

Let (S_{mn}) be a double sequence and $\| \lambda \| = \| \lambda_{pqmn} \|$ $p, q, m, n = 0, 1, 2, 3, \ldots$ a four-dimensional matrix. Then the system of equations

$$t_{pq} = \sum_{m,n=0}^{\infty} \lambda_{pqmn} S_{mn}$$

if the series all converse, transforms (S_{mn}) into a new double sequence (t_{pq}), which shall be called the λ-transform of (S_{mn}). The transformation is said to be *convergence preserving* if the convergence of (S_{mn}) implies that of (t_{pq}) (both in the Pringsheim sense); if in addition the limits are also preserved then the transformation is said to be *regular*. The set of necessary and conditions that $\| \lambda \|$ is convergence preserving or regular have been obtained by Robinson.[4]

The product $\| \lambda\mu \|$ of two matrices $\| \lambda \|$ and $\| \mu \|$ is defined by the relation

$$(\lambda\mu)_{pqmn} = \sum_{r,s=0}^{\infty} \lambda_{pqrs} \mu_{rsmn}$$

The matrix $\| \mu \|$ is said to be a *diagonal matrix* if $\mu_{mnrs} = 0$ $[m \neq r, n \neq s]$ and $\mu_{mnmn} = \mu_{mn}$.

Now let $\triangle$ denote the matrix

$$\triangle_{pqmn} = (-1)^{m+n} \binom{p}{m} \binom{q}{n}.$$

It is easily seen that $\triangle$ is its own reciprocal.

The matrix product $\triangle\mu\triangle$, where μ is a diagonal matrix is called a (four-dimensional) *Hausdorff Matrix*, denoted by (H, μ).

A matrix $\| \lambda \|$ is said to be *factorable* if $\lambda_{pqmn} = \lambda'_{pn} \cdot \lambda''_{qn}$ and this fact is denoted by $\lambda = \lambda' \odot \lambda''$. If the matrix $\| \mu \|$ is also factorable, *i.e.*, $\mu_{mn} = \mu'_m \cdot \mu''_n$ we then have $\triangle \mu \triangle = (\delta \mu' \delta) \odot (\delta \mu'' \delta)$ where $(\delta \mu' \delta)$, $(\delta \mu'' \delta)$ are the two-dimensional Hausdorff matrices.

Now, let $\chi(u, v)$ be a function of bounded variation in the square $(0 \leqslant u \leqslant 1, 0 \leqslant v \leqslant 1)$. Then the sequence μ_{mn} defined by

$$\mu_{mn} = \int_0^1 \int_0^1 u^m \cdot v^n \, d_u d_v \chi(u, v)$$

is called a *moment sequence*.

Without loss of generality we may assume that $\chi(0, 0) = 0$.

If in addition we have that $\chi(1, 1) = 1$ and the continuity conditions

$$\chi(u, +0) = \chi(u, 0), \ \chi(u, +0) = \operatorname*{Lt}_{v \to 0} \chi(u, v)$$

$$\chi(+0, v) = \chi(0, v), \ \chi(+0, v) = \operatorname*{Lt}_{u \to 0} \chi(u, v)$$

are also satisfied, (so that $\mu_{00} = 1$) we shall say that μ_{mn} is a *regular moment constant*.

With the above definition and using the conditions of Robinson,[4] Adams[2] has proved the following theorem—though he does not explicitly state it, in the form here.

THEOREM A1.—*For the class of bounded double sequences the transform defined by* (H, μ) *is regular if and only if* μ_{mn} *is a regular moment constant.*

The notions of inclusion and equivalence are defined for these transformations also, as in the case of simple sequences. The method B is said to *include* another method A if every double sequence summed by the method A is summed by the method B also to the same sum and this fact is denoted by $B \supset A$. If in addition $A \supset B$ then the two methods are said to be *equivalent, i.e.*, $A \sim B$.

For the transformations of double sequences, Adams[1] has proved the following theorem

THEOREM A2.—*Let* $A = A' \odot A''$ *and* $B = B' \odot B''$ *be any two transformations, not necessarily regular, satisfying the conditions* $B' \supset A'$, $B'' \supset A''$ *for simple sequences and* A' *and* A'' *have inverses ; then* $B \supset A$ *for double sequences bounded B- i.e., for the sequences whose B-transforms are bounded.*

This note has for its object to find a necessary and sufficient condition that one Hausdorf matrix may include another, for the case of double sequences with proper restrictions, if needed.

In what follows we shall assume that none of the μ_{mn} vanish.

THEOREM I.—*For the class of double sequences bounded* $\lambda \equiv \triangle\mu\triangle$, *the double sequence transformation defined by* $\lambda' \equiv \triangle\nu\triangle$ *includes* $\lambda \equiv \triangle\mu\triangle$ *if, and only if* ν_{mn}/μ_{mn} *is a regular moment sequence.*

Proof.—Let (S_{pq}) be the double sequence.

Then the λ-transformation of that is given by $\sum_{m,n=0}^{\infty} \lambda_{pqmn} S_{mn}$ which can be regarded as the product of the matrix $\| \lambda \|$ with the matrix $\| S \|$ defined by $S_{mnrs} = 0\,(r, s > 0)$ and $S_{mnoo} = S_{mn}$ and the transformation can be denoted by λS.

Similarly the λ' transformation is $= \lambda' S = \lambda'\,(\lambda^{-1}\lambda)\,S = \lambda'\lambda^{-1}\,(\lambda S)$ (A)

since λ, λ^{-1}, λ' and S are Triangular matrices, and therefore their products are associative.

Now, for λ' to include λ it is necessary and sufficient that $\lambda S \to l$ should imply $\lambda' S$ also $\to l$.

But by hypothesis λS is bounded and every convergent bounded double sequence can be written as λS for a suitable (S) since λ has an inverse which is a lower-semi matrix.

Therefore for λ' to include λ, it is necessary and sufficient from the equation (A) above, that $\lambda'\lambda^{-1}$ is regular for the class of bounded double sequences. This happens if, and only if, ν_{mn}/μ_{mn} is regular moment constant, by virtue of Adams' conditions for Hausdorff transformation to be regular for bounded double sequences.

COROLLARY.—*For the class of double sequences bounded* λ (*or* λ'), $\lambda \sim \lambda'$ *if and only if,* ν_{mn}/μ_{mn} *and* μ_{mn}/ν_{mn} *are both regular moment constants.*

The proof is immediate.

Remarks.—(1) We do not assume that the transformations are regular for any particular class of double sequences.

(2) In the case of factorable transformations of the Hausdorff type we have that the component matrices have inverses; also

$$\mu_{mn} = \mu'_m \cdot \mu''_n \text{ and } \nu_{mn} = \nu'_m \cdot \nu''_n.$$

Besides the above, if we have ν'_m/μ'_m and ν''_n/μ''_n are both regular moment constants then the two-dimensional Hausdorff matrices (h, μ') (h, μ''), (h, ν') and (h, ν'') are such that $(h, \nu') \supset (h, \mu')$ and $(h, \nu'') \supset (h, \mu'')$ by virtue of a known theorem. (Hardy,[3] theorem 209, p. 262), and therefore by the Theorem A2 of Adams stated earlier we have that "If ν'_m/μ'_m and ν''_n/μ''_n are both regular moment constants in the one-dimensional case, then λ' includes λ for the class of double sequences bounded λ'. Thus the hypothesis can be weakened from " *bounded* λ " to " *bounded* λ' ".

(3) For the case of bounded double sequences, the λ-transform is equal to convergence if, and only if, μ_{mn} and $1/\mu_{mn}$ are both regular moment constants.

The proof is immediate from the theorem and its corollary.

Now we shall prove the two-dimensional analogue of the classical theorem due to Mercer: (Hardy,[3] p. 104).

THEOREM II.—*Let* $\alpha > 0$ *and* $\beta > 0$.

$$\text{Let } t_{pq} = \alpha\beta S_{pq} + \frac{\alpha(1-\beta)}{q+1}\sum_{j=0}^{q} S_{pj} + \frac{\beta(1-\alpha)}{p+1}\sum_{i=0}^{p} S_{iq} + \frac{(1-\alpha)}{(p+1)}\cdot\frac{(1-\beta)}{(q+1)}\sum_{i,j=0}^{p,q} S_{ij}$$

Then if (t_{pq}) *is bounded and converges to l, so does* (S_{pq}).

Proof.—We start from

$$\lambda = \Delta\mu\Delta,\ \mu_{mn} = \left(\alpha + \frac{1-\alpha}{m+1}\right)\left(\beta + \frac{1-\beta}{n+1}\right).$$

$$\text{Then } \sum_{m,n=0}^{\infty}\lambda_{pqmn}S_{mn} = \sum_{m,n=0}^{\infty}\left\{\sum_{r,s=0}^{\infty}(-1)^{r+s}\binom{p}{r}\binom{q}{s}\left(\alpha+\frac{1-\alpha}{r+1}\right)\left(\beta+\frac{1-\beta}{s+1}\right)(-1)^{m+n}\cdot\binom{r}{m}\binom{s}{n}\right\}S_{mn}$$

$$= \sum_{m=0}^{p}\left[\sum_{r=m}^{p}(-1)^r\binom{p}{r}(-1)^m\binom{r}{m}\left(\alpha+\frac{1-\alpha}{r+1}\right)\right]\times \times \sum_{n=0}^{q}\left[\sum_{s=0}^{q}(-1)^s\binom{q}{s}(-1)^n\binom{s}{n}\left(\beta+\frac{1-\beta}{s+1}\right)\right]S_{mn},$$

$$= \sum_{m=0}^{p}\left\{\sum_{r=m}^{p}(-1)^r\binom{p}{r}(-1)^m\binom{r}{m}\left(\alpha+\frac{1-\alpha}{r+1}\right)\cdot\left[\beta S_{mq} + \frac{1-\beta}{q+1}(S_{m0}+S_{m1}+\ldots.+S_{mq})\right]\right\}$$

[since the one-dimensional Mercerian Transform (h, μ'') is transformation with $\mu''_n = \beta + \frac{1-\beta}{n+1}$],

$$= \alpha\beta\, S_{pq} + \frac{(1-\beta)}{q+1} \cdot \alpha\,(S_{p0} + S_{p1} + \ldots + S_{pq})$$

$$+ \frac{(1-\alpha)}{p+1} \cdot \beta\,(S_{0q} + S_{1q} + \ldots + S_{pq})$$

$$+ \frac{(1-\alpha)}{p+1} \cdot \frac{(1-\beta)}{q+1} \begin{bmatrix} S_{00} + S_{10} + \ldots + S_{p0} \\ + S_{01} + S_{11} + \ldots + S_{p1} \\ + \ldots\ldots\ldots\ldots\ldots \\ + S_{0q} + S_{1q} + \ldots + S_{pq} \end{bmatrix}$$

$$= \alpha\beta S_{pq} + \alpha \cdot \frac{(1-\beta)}{q+1} \cdot \sum_{j=0}^{q} S_{pj} + \frac{\beta(1-\alpha)}{p+1} \sum_{i=0}^{p} S_{iq}$$

$$+ \frac{(1-\alpha)(1-\beta)}{(p+1)(q+1)} \sum_{i,j=0}^{p,q} S_{ij}$$

But this is the expression for (t_{pq}) by definition.

Thus (t_{pq}) is the $\triangle\mu\triangle$ transformation of (S_{pq}) with

$$\mu_{mn} = \left(\alpha + \frac{1-\alpha}{m+1}\right)\left(\beta + \frac{1-\beta}{n+1}\right) = \mu'_m \cdot \mu''_n \text{ say.}$$

It has been proved (*vide* Hardy,[3] p. 264) that both μ'_m and $1/\mu'_m$ as well as μ''_n and $1/\mu''_n$ are regular moment constants in the one-dimensional case for $\alpha > 0$ and $\beta > 0$ respectively. Therefore μ_{mn} and $1/\mu_{mn}$ are both regular moment constants and hence by remark 3 of the previous theorem the result follows immediately.

In conclusion I acknowledge with grateful pleasure the help and guidance of Prof. V. Ganapathy Iyer in the preparation of this paper.

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STUDIES IN THE ISOQUINOLINE SERIES

Part I. Synthesis of 1-Benzyl Isoquinoline Derivatives

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The remarkable ease of oxidation of 1-benzyl-3 : 4-dihydroisoquinolines was first observed by Buck, Haworth and Perkin,[1] who carried out a study of the oxidation of compounds of this type bearing alkoxy groups in the benzyl portion of the molecule. However 3 : 4-dihydro-1-(2′-nitrobenzyl)-isoquinoline derivatives, several of which have been prepared in connection with aporphine syntheses, are remarkably stable as first observed by Gulland and Haworth.[2] In connection with a study of the mechanism of oxidation of 1-benzyl-3 : 4-dihydroisoquinoline derivatives, we had occasion to synthesise a number of compounds belonging to this class, with varying substituents in the benzyl portion of the molecule. The dihydroisoquinolines were made by cyclisation of arylacetyl derivatives of homovera-trylamine by the classical Bischler-Napieralski method, with phosphorus oxychloride in boiling toluene or phosphorus pentachloride in cold chloroform. The last reagent invariably gave higher yields of cleaner products. The dihydroisoquinolines were also reduced to the corresponding tetrahydroisoquinolines for purposes of pharmacological examination. We record here the data on the compounds prepared in the course of this study. A study of the oxidation of these dihydroisoquinolines will be reported in another paper.

Experimental Procedure

Phenylacetic acids

The phenylacetic acids employed in this study were prepared by procedures already described in literature.

N-β-(3′ : 4′-Dimethoxyphenethyl)-phenylacetamides

The amides were made by the procedure of Gulland and Haworth.[2] The amides are listed in Table I and the yields reported are those obtained by this method. The amides could also be made by the following alternative procedure, illustrated in the case of N-2-Bromo-β-(3′ : 4′-dimethoxyphenethyl)-phenyl-acetamide.

TABLE I

N-β-(3′: 4′-Dimethoxyphenethyl)-Acetamides

Substituted phenylacetamides	Mol. Formula	M.P. °C.	Yield %	% Nitrogen	
				Found	Required
Nil	$C_{18}H_{21}O_3N$	108	65	4·70	4·68
2-Br	$C_{18}H_{20}O_3NBr$	128	84	4·14	3·70
3-Br	$C_{18}H_{20}O_3NBr$	105–6	76	3·79	3·70
4-Br	$C_{18}H_{20}O_3NBr$	129	81	4·12	3·70
2-Me	$C_{19}H_{23}O_3N$	123–24	94	4·57	4·47
3-Me	$C_{19}H_{23}O_3N$	92–93	85	4·81	4·47
4-Me	$C_{19}H_{23}O_3N$	121	84	4·82	4·47
2-OMe	$C_{19}H_{23}O_4N$	119–20	81	4·47	4·26
3-OMe[3]	$C_{19}H_{23}O_4N$	114	82	4·54	4·26
4-OMe[4]	$C_{19}H_{23}O_4N$	124–25	94	4·46	4·26
2-Nitro[2]	$C_{18}H_{20}O_5N_2$	110–11	86	8·45	8·14
3-Nitro	$C_{18}H_{20}O_5N_2$	132–33	78	8·40	8·14
4-Nitro[5]	$C_{18}H_{20}O_5N_2$	119–20	86	8·00	8·14
4-Cyano	$C_{19}H_{20}O_3N_2$	131–32	61	8·75	8·64

A mixture of 2-bromophenylacetic acid (5·5 g.) and homoveratrylamine (5 g.) was heated at 180–200° in an oil-bath for one hour. After cooling, the solid was broken up, ground successively with dilute hydrochloric acid (2N) and dilute sodium hydroxide solution (2N), filtering after each operation and finally washed with water. The residue after drying in a desiccator weighed 8 g. and melted at 128°.

1-Benzyl-3: 4-dihydro-6: 7-dimethoxyisoquinolines

The amides were cyclised to the 3: 4-dihydroisoquinolines by either of the following procedures:

(*a*) *Cyclisation with phosphorus oxychloride.*—A suspension of the amide (1 g.) in dry toluene (10 c.c.) was refluxed for two hours with phosphorus oxychloride (3 c.c.). The solution was then poured on to crushed ice and

after decomposition of the excess phosphorus oxychloride, the aqueous layer was separated and extracted with ether for removal of non-basic impurities. The aqueous layer was then cooled well, and made basic with sodium hydroxide solution in an atmosphere of hydrogen. The liberated base was rapidly extracted with ether and the ether extract was dried over potassium hydroxide. The dry ether extract was saturated with dry hydrogen chloride gas and the precipitated hydrochloride was filtered, washed with ether and recrystallised from an alcohol-ether mixture.

In the case of N-(3′: 4′-dimethoxyphenethyl)-2-nitrophenyl-acetamide, the cyclisation was effected by leaving the amide in toluene solution with

TABLE

1-*Benzyl*-6 : 7-*dimethoxy*-

Substituent	Hydrochloride					
	Mol. Formula	M.P. °C.	Yield %		% Nitrogen	
			$POCl_3$	PCl_5	Found	Required
Nil	$C_{18}H_{20}O_2NCl$	182	70	84	4·40	4·40
2–Br	$C_{18}H_{19}O_2NClBr$	197 (decomp.)	73	91	3·66	3·53
3–Br	$C_{18}H_{19}O_2NClBr$	190	69	78	3·70	3·53
4–Br	$C_{18}H_{19}O_2NClBr$	175	73	91	3·19	3·53
2–Me	$C_{19}H_{22}O_2NCl$	186	71	90	4·33	4·22
3–Me	$C_{19}H_{22}O_2NCl$	111–12	68	85	4·29	4·22
4–Me	$C_{19}H_{22}O_2NCl$	196–97 (decomp.)	66	88	4·55	4·22
2–OMe	$C_{19}H_{22}O_3NCl$	169–70	75	80	3·98	4·03
3–OMe	$C_{19}H_{22}O_3NCl$	183	76	76	4·40	4·03
4–OMe	$C_{19}H_{22}O_3NCl$[4]	165	71	90	4·24	4·03
2–Nitro	$C_{18}H_{19}O_4N_2Cl$[2]	218 (decomp.)	82	95	7·52	7·73
3–Nitro	$C_{18}H_{19}O_4N_2Cl$	190	76	88	7·64	7·73
4–Nitro	$C_{18}H_{19}O_4N_2Cl$	180–81	85	99	7·66	7·73
4–Cyano	$C_{19}H_{19}O_2N_2Cl$	209–11	76	79	8·04	8·18

phosphorus oxychloride at room temperature, the product being worked up as described earlier.

(*b*) *Cyclisation with phosphorus pentachloride.*—A solution of the amide (1 g.) in dry chloroform (10 c.c.) was treated cautiously with phosphorus pentachloride (1·3 g.) and left for 48 hours protected from moisture. The chloroform was removed *in vacuo* and the residue treated with crushed ice. The acid solution was worked up as earlier to yield the base hydrochloride.

The data relating to the yields of the dihydroisoquinolines and the physical constants of the hydrochlorides and the picrates are recorded in Table II.

II

3 : 4-*dihydroisoquinolines*

Picrate			
Mol. Formula	M.P. °C.	% Nitrogen	
		Found	Required
$C_{24}H_{22}O_9N_4$	176	10·70	11·00
$C_{24}H_{21}O_9N_4Br$	183	9·60	9·51
$C_{24}H_{21}O_9N_4Br$	183–84 (decomp.)	9·90	9·51
$C_{24}H_{21}O_9N_4Br$	197–98 (decomp.)	9·97	9·51
$C_{25}H_{24}O_9N_4$	192	10·84	10·69
$C_{25}H_{24}O_9N_4$	193–94 (decomp.)	10·77	10·69
$C_{25}H_{24}O_9N_4$	182–83 (decomp.)	11·04	10·69
$C_{25}H_{24}O_{10}N_4$	164–66	10·53	10·37
$C_{25}H_{24}O_{10}N_4$	156–57	10·74	10·37
$C_{25}H_{24}O_{10}N_4$[4]	168–69 (decomp.)	10·10	10·37
$C_{24}H_{21}O_{11}N_5$	195–97 (decomp.)	13·00	12·61
$C_{24}H_{21}O_{11}N_5$	197–98 (decomp.)	12·88	12·61
$C_{24}H_{21}O_{11}N_5$	193–94	12·97	12·61
$C_{25}H_{21}O_9N_5$	200–2 (decomp.)	12·75	13·08

TABLE III

1-Benzyl-1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethoxyisoquinolines

Substituent	Hydrochloride				Picrate			
	Mol. Formula	M.P. °C.	% Nitrogen		Mol. Formula	M.P. °C.	% Nitrogen	
			Found	Required			Found	Required
2–Br	$C_{18}H_{21}O_2NClBr$	215–16	3·13	3·51	$C_{24}H_{23}O_9N_4Br$	181–82	9·68	9·48
3–Br	$C_{18}H_{21}O_2NClBr$	225–27	3·72	3·51	$C_{24}H_{23}O_9N_4Br$	155	9·19	9·48
4–Br	$C_{18}H_{21}O_2NClBr$	213–14	3·37	3·51	$C_{24}H_{23}O_9N_4Br$	180 (Sintering at 165)	9·70	9·48
2–Me	$C_{19}H_{24}O_2NCl$	196–98	3·84	4·20	$C_{25}H_{26}O_9N_4$	184–85	10·61	10·64
3–Me	$C_{19}H_{24}O_2NCl$	208–10	4·51	4·20	$C_{25}H_{26}O_9N_4$	171–72	10·40	10·64
4–Me	$C_{19}H_{24}O_2NCl$	222–24	3·78	4·20	$C_{25}H_{26}O_9N_4$	173–75	10·60	10·64
2–OMe	$C_{19}H_{24}O_3NCl$	176–78	3·83	4·01	$C_{25}H_{26}O_{10}N_4$	155–56	10·24	10·33
4–OMe	$C_{19}H_{24}O_3NCl$[4]	195–97	4·07	4·01	$C_{25}H_{26}O_{10}N_4$	148–50	10·13	10·33
2–NH_2	$C_{18}H_{24}O_2N_2Cl_2$	220 (decomp.)	7·57	7·55	$C_{30}H_{28}O_{16}N_8$	gum	..	..
3–NH_2	$C_{18}H_{24}O_2N_2Cl_2$	237–39 (decomp.)	7·41	7·55		198 (decomp.)	14·57	14·81
4–NH_2	$C_{18}H_{24}O_2N_2Cl_2$	233 (decomp.)	7·28	7·55	$C_{30}H_{28}O_{16}N_8$	181–82 (decomp.)	14·50	14·81

1-Benzyl-1 : 2 : 3 : 4-Tetrahydro-6 : 7-dimethoxyisoquinolines

The three nitrobenzyl-dihydroisoquinolines could not be reduced successfully by catalytic reduction. In these cases, the dihydroisoquinoline hydrochloride (1 g.) dissolved in concentrated hydrochloric acid (20 c.c.) and water (10 c.c.) was treated with zinc dust (6 g.) at 60–70° with stirring. After two hours, the solution was filtered, cooled strongly, made alkaline and extracted with benzene. The benzene extract after drying over potassium hydroxide, was saturated with dry hydrogen chloride gas. The dihydrochloride was filtered and crystallised from absolute alcohol-ether mixture.

All the other dihydroisoquinoline hydrochlorides were reduced in alcoholic solution with Adams' catalyst at a pressure of 60 lb. per sq. inch. After filtering off the catalyst, the solvent was removed, yielding the tetrahydroisoquinoline hydrochlorides in nearly quantitative yield. Further purification was effected by crystallisation from absolute alcohol.

The tetrahydroisoquinolines are listed in Table III.

Summary

A series of 1-benzyl-3 : 4-dihydro-6 : 7-dimethoxy-, and 1-benzyl-1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethoxyisoquinolines with varying substituents in the benzyl portion of the molecule, and their derivatives are reported.

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STUDIES ON CUTICLES OF ARTHROPODS

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1. Introduction

The present investigation was undertaken in connection with a study of the cuticles of Arthropods being made by Dr. Krishnan of the Zoology Department of this University. During his studies on Scorpion, he found that the epicuticle was different from what is normally found in insects. An X-ray picture taken of this material in this laboratory confirmed this and the picture was published by Krishnan (1954) before a detailed examination was made of it and he described it as indicating the presence of a new form of protein in the epicuticle. However, a more detailed study of this material revealed that it was chitinous and consisted largely of chitin. This was a surprising result and in consequence, a detailed X-ray study was made of the cuticles of a number of species of Arthropods. The results of these studies are presented here. The specimens were all prepared and supplied by Dr. Krishnan, to whom the author is deeply grateful. The histological studies of these, together with a discussion of the zoological matters connected with them, are being published by him elsewhere (Krishnan, 1955).

The cuticle of Arthropods consists essentially of two different layers. The outer layer, called the epicuticle, is supposed to be a lipo-protein membrane and is said to contain no chitin. The inner layer, called the procuticle, is said to contain chitin (Richards, 1951). In insects, the epicuticle is further subdivided into an inner basal layer composed of lipo-proteins, overlaid by an outer paraffin layer (Dennell, 1946). The procuticle or the chitinous part of the cuticle may also be subdivided into the exo- and endo-cuticles of which the former gets tanned in the latter stages of development. (Frænkel and Rudall, 1947). A generalised scheme of the subdivision is given below following mainly the scheme adopte d by Richards (1951):

- Cuticle
  - Epicuticle (Non-chitinous)
    - Lipid epicuticle (Wax layer)
    - Protein epicuticle
  - Procuticle (Chitin-Protein)
    - Exocuticle (Sclerotized, may also be calcified)
    - Endocuticle (may also be calcified)

It has been assumed in the above classification that the epicuticle of all Arthropods is devoid of chitin, like the insect epicuticle. Richards (1951) in fact has titled the chapters in his book which deal with the two layers of the cuticle as "The Epicuticle or Non-chitinous cuticle" and "The Procuticle or Chitinous cuticle".

The epicuticle of Arthropods other than insects has so far received little attention and there is considerable uncertainty regarding the homology of the epicuticle. It is therefore to be hoped that the results of the present study would be of value in obtaining a proper classification. The cuticles of the following species representative of the principal classes of the phylum have been studied:

A. *Palamneus Swammerdami* .. (Arachnida)
B. *Scolopendra Subspinepes* .. (Myriopoda)
C. *Blatta Orientalis* .. .. (Insecta)
D. *Peneaus Indicus* .. .. (Crustacea)
E. *Propallene Kempi* .. .. (Pycnogonida)

2. Materials and Experimental Methods

Studies were made both of the entire cuticle and of the epicuticle. The epicuticle was separated from the rest of the cuticle by treatment with concentrated nitric acid or in some cases chlorated nitric acid. To obtain X-ray photographs, two methods of mounting were adopted. In the case of thick materials like the entire cuticle of scorpion, the layer (about 2 mm. $\times$3 mm.) was fixed on to a fibre and mounted on a goniometer. X-ray patterns could thus be readily taken with the surface either perpendicular or parallel to the beam. With very thin membranes like the epicuticle, they were fixed over a small hole (2 mm. in diameter), drilled in a brass sheet and the latter was mounted on a goniometer. Photographs could only be obtained perpendicular to the surface in this case. Several layers of the membrane could be put one over the other if necessary. For obtaining pictures with the beam parallel to the surface, the first method was used even with thin membranes.

Chitin prepared from crab shells was used as control. The crab shells were treated with dilute nitric acid, then with 20 per cent. sodium hydroxide, washed and finally dried with alcohol and ether. In all these operations, the membranes were carefully preserved intact.

3. Results of the Investigation

In this section, we shall briefly describe the photographs obtained, pointing out the salient facts with reference to the Figs. 1–12, Plates II and III.

The measurements are summarised in Tables I and II and the data will be critically analysed in the next section.

A. *Palamneus Swammerdami* (Scorpion)

(i) *Entire cuticle.*—The diffraction pattern of the entire cuticle of *Palamneus Swammerdami* taken with the beam normal to the surface (Fig. 1, Plate II) showed a pattern similar to that of purified chitin, in consisting of three prominent rings at about 10·3 A, 4·6 A and 3·4 A. The line at 10·3 A is diffuse and the spacing is distinctly larger than that for pure chitin, namely 9·6 A. The latter agrees with the data of Meyer and Pankow (1935) for chitin. The pattern is essentially due to the procuticle, since the epicuticle is a very thin layer, and it agrees in all respects with that reported for insect entire cuticles by Frænkel and Rudall (1940, 1947). An X-ray photograph was also taken with the beam parallel to the surface (not reproduced). This again agrees completely with the pattern given by insect entire cuticle (Frænkel and Rudall, 1947).

TABLE I

Measurements of patterns normal to the surface of entire cuticles

	Chitin		Scorpion		Centipede*		Cockroach		Peneaus† (clear region)		Pycnogonid	
θ	*d*	Int.	*d*	Int.	*d*	Int.	*d*	Int.	*d*	Int.	*d*	Int.
4° 37′	9·6	v.s.	10·3	s. diff.	10·3	s. diff.	diffuse		diffuse		diffuse	
6° 29′	6·86	w.										
8° 53′	5·02	w.	5·12	w. diff.			5·15	v.w.	5.15	v.w.		
9° 39′	4·62	s.	4·62	s.	4·62	m.	4·62	s.	4·62	s.	4·62	m.
10° 24′	4·29	v.w.										
11° 38′	3·84	v.w.										
13° 17′	3·37	v.s.	3·37	s.	3·41	s.	3·37	s.	3·41	s.	3·37	s.
14° 38′	3·07	v.w.										
16° 19′	2·76	v.w.										
17° 30′	2·58	w.										

* In addition, sharp rings were observed corresponding to *d*- values of 2·48 (v.w.), 2·36 (w), 2·15 (v.s.), 2·08 (s.) and 1·85 (m.).

† In the opaque regions, the ring at 3·4 A shifts to 3·5 A and additional rings were also found at 3·21 A (m.), 2·83 A (s.), 2·60 A (m.), 2·33 A (w.), 2·28 A (w.), 1·96 A (w.), 1·84 A (w.), 1·73 A (w.) and 1·47 A (w.).

(ii) *Epicuticle.*—The diffraction patterns taken with the X-ray beam both perpendicular and parallel to the surface of the epicuticle are shown

in Figs. 8 and 11 (Plate III). The spacings observed are identical with those found for chitin. In particular, the 10·3 A line comes down to 9·6 A, the same as for chitin. Although there is perfect agreement in the spacings of the pattern with those of pure chitin, the 4·6 A line, which is very intense in chitin, is found to be weak in the pattern of the epicuticle. The general appearance of the two patterns are seen to be quite different, as may be verified by comparing Figs. 6 and 8 (Plates II and III). In fact, this striking difference showed up even before the epicuticle was freed of all endocuticular matter (Fig. 9). However, the patterns taken with the beam parallel to the surface do not reveal any sharp differences between the scorpion epicuticle and pure chitin (Figs. 11 and 12, Plate III). The implications of the alteration in the relative intensities of the different lines noticed in the pattern of the epicuticle are discussed in Section 4. It must be mentioned that the epicuticle, as first prepared, showed a number of sharp intense extra lines with spacings of 2·22 A, 2·44 A, 3·7 A and 4·14 A (Fig. 7, Plate III) but these disappeared when it was treated with toluene. These spacings are identical with those obtained for long chain hydrocarbons (C_{29} or thereabouts). The prominent lines for $C_{29}H_{60}$ are 2·20 A (m.), 2·48 A (m.), 2·75 A (v.w.), 3·72 A (v.s.) and 4·15 A (v.s.) (Muller, 1928). This shows that there is a thin waxy layer even outside the epicuticle. The presence of such a thin membrane of lipoids was detected by Krishnan (1954) by chemical tests, but the X-ray pattern has enabled us to identify it as a long chain saturated hydrocarbon.

The identity of spacings observed in the epicuticle with those of chitin suggests that the epicuticular material is built on a chitin lattice and is most probably a chitin-protein complex. In view of the fact that chitin was formerly considered to be absent in arthropod epicuticles, it was considered necessary to have an independent confirmation. This was obtained by hydrolysing the epicuticular material with 4 N hydrochloric acid and estimating the liberated glucosamine by the method of Elson and Morgan (1933) as modified by Palmer, Smyth and Meyer (1937). The experimental procedure was identical with the one adopted by the latter authors. The amount of glucosamine in 19·7 mg. of the epicuticular material was found to be 1·196 mg. or 0·06069 mg./mg. A duplicate of the experiment was carried out with pure chitin (B.D.H.), and the value obtained was 1·298 mg. in 17·73 mg. of chitin or 0·0732 mg./mg.* These values indicate that the

* It is of interest to observe that chitin gets hydrolysed only to a limited extent by 4 N hydrochloric acid as shown by the value of liberated glucosamine. Hence the need for a duplicate experiment with authentic chitin. The value reported here agrees with the value reported by Hackman (1954).

epicuticle is largely composed of chitin, containing in fact 83% by weight of chitin.

In order to determine the nature of the substance other than chitin present in the epicuticle, another portion of the hydrolysate was subjected to chromatographic analysis after removal of hydrochloric acid by repeated distillation under vacuum. The method of ascending chromatography (Radhakrishnamurthy and Sarma, 1952) was employed and the solvents were the same as used by them. The chromatogram, after colour development with ninhydrin, showed the presence of a spot with an R_f value of 0·26 which agreed with that of L (+) glutamic acid. This indicates that protein is present in the scorpion epicuticle, although its precise nature has not yet been ascertained.

TABLE II

Measurements of X-ray patterns of epicuticles of Scorpion and Centipede—beam normal to surface

Scorpion†		Centipede		Chitin	
d	Int.	*d*	Int.	*d*	Int.
9·45	v.s.	9·4	v.s.	9·6	v.s.
6·86	w.			6·86	w.
5·02	w.			5·02	w.
4·62	w.	4·62	w.	4·62	v.s.
				4·29	v.w.
3·84	v.w.			3·84	v.w.
3·37	s.	3·41	s.	3·37	s.
3·07	v.w.	3·07	w.	3·07	v.w.
2·76	w.	2·76	w.	2·76	v.w.
2·58	m.	2·58	w.	2·58	w.

† In the epicuticle not treated with toluene, lines with the following *d*-values were also found: 2·22 (m), 2·44 (m), 2·89 (w), 3·67 (v.s.) and 4·14 (v.s.).

B. *Scolopendra* (Centipede)

(i) *Entire cuticle.*—The diffraction pattern normal to the surface (Fig. 2, Plate II) reveals the presence of prominent lines identical with those found for scorpion and insect entire cuticles. As in the case of scorpion, the 10·3 A ring is very diffuse and is shifted towards the centre of the pattern with reference to pure chitin. In addition, rings with spacings of 2·48 A (v.w.), 2·36 A (w.), 2·15 A (v.s.), 2·08 A (s.), 1·85 A (m.), are also seen (not found in Fig. 2 being too large) which it has not been possible to

definitely identify. Treatment with potassium hydroxide caused the disappearance of the extra lines and further led to some changes in the main pattern itself. Potassium hydroxide treatment is known to remove the protein from the endocuticle, leaving only chitin (Frænkel and Rudall, 1947). In scolopendra also, the potassium hydroxide-treated specimen gave an X-ray pattern very similar to pure chitin. In particular, the 10·3 A line became sharper and corresponded to a spacing of 9·6 A, in agreement with pure chitin.

(ii) *Epicuticle.*—The diffraction pattern of the epicuticle of *Scolopendra* is largely similar to that of *Palamneus*, showing lines at spacings corresponding to pure chitin. In this case also, the intensities of the various lines do not agree with those of pure chitin. As was found with the scorpion epicuticle, the 4·6 A line is weak and the X-ray photograph is closely similar to that given by scorpion epicuticle (compare Figs. 9 and 10, Plate III). Thus it would appear that the particular type of protein-chitin complex found in scorpion is not an exception but may also occur in other genera.

C. *Blatta Orientalis* (cockroach)

(i) *Entire cuticle.*—The study of cockroach was taken up as a sort of control as it belongs to the class *Insecta*, which have been thoroughly investigated. The diffraction pattern of the entire cuticle of cockroach (Fig. 3, Plate II) is exactly similar to that given by the other entire cuticles studied, and agreed with that reported by Frænkel and Rudall (1947). The 10 A ring is very diffuse and could not be clearly seen.

(ii) *Epicuticle.*—The epicuticle of insects is devoid of chitin and is known definitely to contain only protein, and this situation would be expected in cockroach. The X-ray pattern of the cockroach epicuticle does not show any details except a central halo. Thus chitin is definitely not present in the epicuticle in this case, which apparently is made up of protein alone. However the pattern does not agree with that given by arthropodin, which is the protein constituent of the endocuticle (Frænkel and Rudall, 1947).

D. *Peneaus Indicus*

(i) *Entire cuticle.*—The diffraction pattern of the clear and transparent regions of the entire cuticle of *Peneaus* (Fig. 4, Plate II) shows the presence of the same rings as those found in other entire cuticles, and as with others, the 10·3 A line is found to be diffuse and shifted towards the centre, compared to pure chitin. Certain regions of the cuticle are however found to be opaque due to a white deposit and the diffraction pattern of those

regions exhibits a number of extra lines. The nature of this component is under further investigation and the pattern is not reproduced here.

(ii) *Epicuticle.*—The pattern does not show any details but only exhibits a central halo indicating the absence of chitin.

E. *Pycnogonida*

(i) *Entire cuticle.*—The pattern (Fig. 5, Plate II) is again similar to that given by entire cuticles of insects and other species studied. Here also the 10·3 A line is found to be diffuse and shifted towards the centre with respect to pure chitin. The pattern does not indicate the presence of any other crystalline component. Thus the endocuticle is found to conform to the standard type found in all arthropods.

(ii) *Epicuticle.*—The pattern, like those of cockroach and *Peneaus*, does not reveal any structure indicating the absence of chitin in the epicuticle.

4. DISCUSSION

A common feature found with all the cuticles studied is that the diffraction patterns of the entire cuticle are very similar in all the cases, and agree with the pattern observed by Frænkel and Rudall (1947) for the entire cuticle of the stick insect. Since the epicuticle is a very thin membrane, the pattern is essentially that due to the exocuticle and endocuticle. Thus it appears that the endocuticle has the same constitution in all Arthropoda. The characteristic differences between the patterns of the endocuticle and that of pure chitin are:

(1) The 9·6 A reflection in the cuticle is particularly diffuse and displaced towards the centre with respect to that of chitin to 10·3 A.

(2) There is a pronounced fogging in the centre of the photograph within the 9·6 A ring.

(3) The diffuseness or breadth of the 9·6 A spacing, which corresponds to 002 of chitin, is also shown in the picture taken with the beam parallel to the surface. The other spots in this setting are not appreciably more diffuse than in pure chitin.

All these features are in accord with the findings of Frænkel and Rudall (1947) who have interpreted that the peculiar and characteristic pattern of the insect cuticle is due to an intimate association of chitin and protein chains. According to them, the protein occurs in the fully extended β-configuration and in this configuration the length of three residues of the polypeptide chain in the protein is very nearly equal to the length of two chitobiose units along the *b*-axis (= 10·46 A). Thus the two could fit

very well. The occurrence of the protein chains results in a slight swelling of the chitin structure along the *c*-axis, and the spacing of 002 increases from 9·6 A to about 10·3 A and is also variable, resulting in the diffuseness of the corresponding ring. The 020 spacing on the other hand does not show any appreciable change, although it is slightly more diffuse than in pure chitin. The fact that the 002 spacing is particularly increased shows that the protein chains must occur in between the chitin chains along this direction. For instance they might also run parallel to the *a*-axis in between the chitin chains, as has been recently pointed out by Rudall (1950).

The most important finding of the present study is the fact that chitin occurs in the epicuticle of scorpion and centipede. A preliminary note regarding this is under publication in *Nature* (Krishnan, Ramachandran and Santhanam, 1955). Previously it has been thought that the epicuticle is entirely devoid of chitin. On the other hand, the occurrence of chitin in the epicuticle is not common to all arthropods. For instance, it is found that chitin is definitely absent in the epicuticles of cockroach, *Peneaus* and the pycnogonid, and that it is entirely made up of protein in these cases. Krishnan (1955) finds that the epicuticles in these are hardened by phenolic tanning, while such a tanning does not occur in the chitinous epicuticles, although they also contain protein. Thus it would be necessary to revise some of the current ideas regarding the homology of epicuticles, and to consider that the epicuticle may be of two types, either containing chitin or devoid of it.

Thus in the epicuticle of scorpion and centipede, we have a new type of protein-chitin complex distinct from the complex found by Frænkel and Rudall in the endocuticle. Here the pattern agrees almost entirely with pure chitin pattern except for the fact that the 200 reflection (4·6 A spacing line), which is strong in chitin, is found to be weak. The spacings however are practically unaffected.

This alteration in the relative intensities of the different lines could be attributed either to the presence of an impregnating material like a protein, or merely to the physical condition, *i.e.*, the degree of orientation of the chitin fibres in the membrane. The latter possibility was readily eliminated. The pattern of chitin shown in Fig. 6, Plate II was obtained from the cuticle of crab, treated so as to remove all other materials, but carefully preserving the membrane intact. It would be expected that the chitin fibres would all be oriented parallel to the plane of the lamina though in random directions in the plane. Here the 4·6 A line and 3·4 A line have about the same relative intensity. If the orientation is made completely

random by taking a photograph of the *powdered* material, then the 4·6 A line became more intense than the 3·4 A line. The same result could be obtained by rotating the membrane about an axis perpendicular to the X-ray beam having first set it normal to the beam. The 4·6 A line then became more intense than the 3·4 A line near the equator. Now in the diffraction pattern of the epicuticle kept normal to the beam, the 4·6 A line was much weaker than the 3·4 A line, which is different from that observed with crab chitin membrane. On rotating the epicuticle as in the experiment described just now, the two became of comparable intensity near the equator, while with pure chitin, the 4·6 A line was much more intense. Thus we can conclude that the weakening of the 200 reflection is really due to the presence of some extraneous material, probably protein, in the chitin lattice. The protein chains are so situated that the 200 reflection alone is weakened. This could be explained if the protein chains are assumed to occur midway between the layers of chitin chains which are spaced $a/2$ from one another. It is very significant that, in this chitin-protein combination, the 002 reflection does not show any diffuseness or shift towards the centre. This is presumably due to the small percentage, about 10%, of protein present as contrasted with the endocuticle where it may be as high as 50%. On the other hand, the binding between the chitin and protein must be very strong indeed in the epicuticle, since the epicuticle is unaffected by treatment with concentrated nitric acid or chlorated nitric acid for long periods of time. The epicuticle does not also give a definite positive chitosan test, although it remains intact after the treatment with boiling potassium hydroxide, as shown by Krishnan in his histochemical studies. He also found by the same method evidence for S-S-bonded proteins, as shown by the disruptive effect produced by the addition of alkaline sodium sulphide (Krishnan, 1955). That the protein in the epicuticle does not occur in a loosely bound form, but is incorporated in the chitin lattice is also shown by the fact that the region inside the 9·6 A ring is clear, unlike in the pattern of the entire cuticle where it is highly fogged. (This is particularly well seen in the original negatives.)

At the present stage, the author is not in a position to say precisely what is the nature of the association between chitin and protein in the epicuticular material. Presumably the type of association pictured by Frænkel and Rudall (1947) really occurs in this case, as shown by the appreciable weakening of the 200 reflection. The protein chains may run midway between two chitin chains which are separated by $a/2$. On the other hand the protein chains may run in a direction perpendicular to the chitin chains as suggested by Rudall (1950) in the endocuticular material. This is suggested by the fact

that the *c* spacing is particularly affected. However these suggestions are very tentative and more precise models are being built up to verify them.

Acknowledgement

The author wishes to record his deep indebtedness to Prof. G. N. Ramachandran for the invaluable suggestions he gave and the keen interest he took in the course of this study. His thanks are also due to Prof. P. S. Sarma for facilities provided for chromatographic work and to the University of Madras for the award of a research fellowship.

Summary

The paper deals with a study of cuticles of Arthropods by X-ray and chemical methods. It is shown that the endocuticular constitution is the same in all the animals studied, conforming to the chitin-protein complex observed by Frænkel and Rudall. The epicuticle on the other hand showed wide variations. In scorpion and centipede, the epicuticle was found to consist largely of chitin, which was entirely unexpected. In other cases, no chitin was present in the epicuticle in agreement with the current ideas of the constitution of the epicuticle. The nature of the association between protein and chitin in the epicuticular material is also discussed.

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DESCRIPTION OF PLATES

PLATE II

FIG. 1. X-ray photograph of entire cuticle of scorpion. Beam normal to surface.

FIG. 2. X-ray photograph of entire cuticle of centipede. Beam normal to surface.

FIG. 3. X-ray photograph of entire cuticle of cockroach. Beam normal to surface.

FIG. 4. X-ray photograph of entire cuticle of *Peneaus*. Beam normal to surface.

FIG. 5. X-ray photograph of entire cuticle of a Pycnogonid. Beam normal to surface.

FIG. 6. X-ray photograph of chitin prepared from crab shell. Beam normal to surface.

All photographs correspond to a specimen to film distance of 5 cm.

PLATE III

FIG. 7. X-ray photograph of epicuticle of scorpion with the waxy layer. Beam normal to surface.

FIG. 8. X-ray photograph of epicuticle of scorpion completely purified. Beam normal to surface.

FIG. 9. X-ray photograph of epicuticle of scorpion incompletely purified. Beam normal to surface.

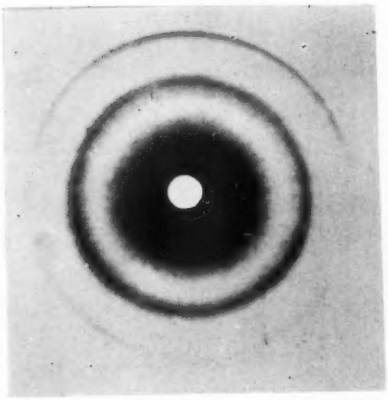
FIG. 10. X-ray photograph of epicuticle of centipede. Beam normal to surface.

FIG. 11. X-ray photograph of epicuticle of scorpion. Beam parallel to surface.

FIG. 12. X-ray photograph of chitin. Beam parallel to surface.

Specimen-film distance equal to 5 cm. for all photographs.

FIG. 1



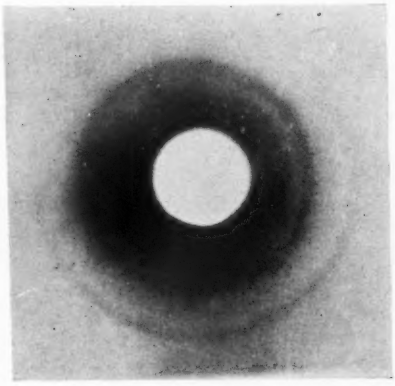
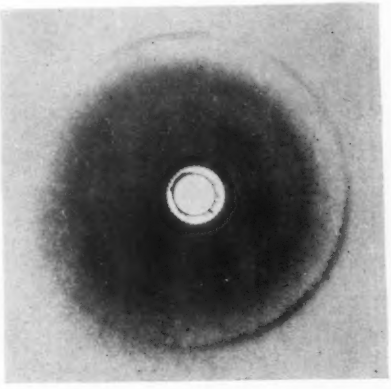


FIG. 2

FIG. 3



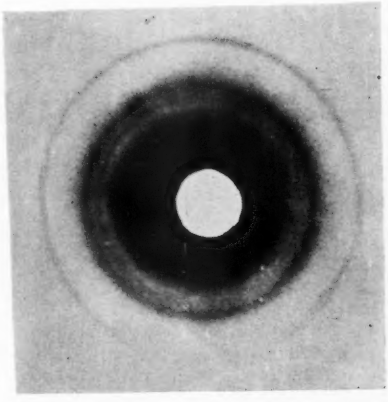
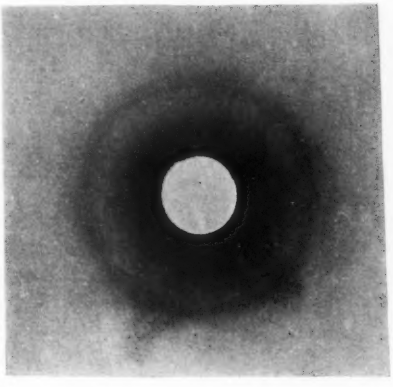


FIG. 4

FIG. 5



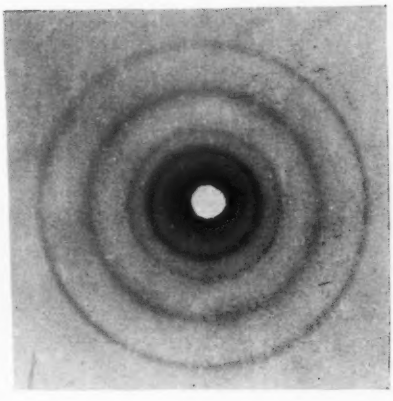


FIG. 6

FIG. 7

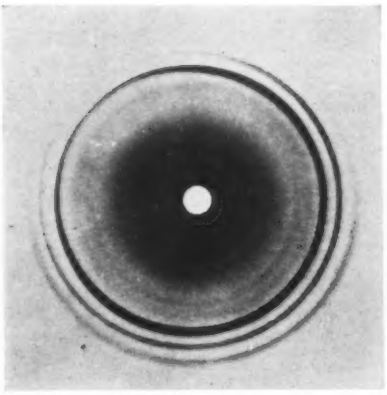


FIG. 8

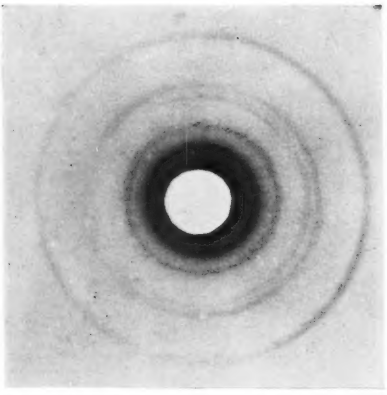


FIG. 9

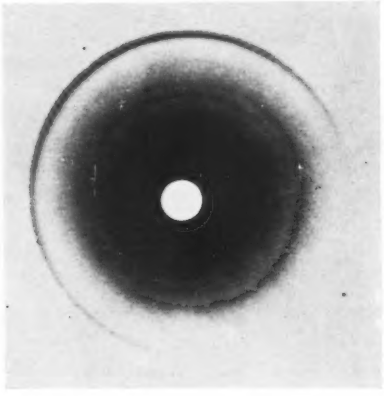


FIG. 10

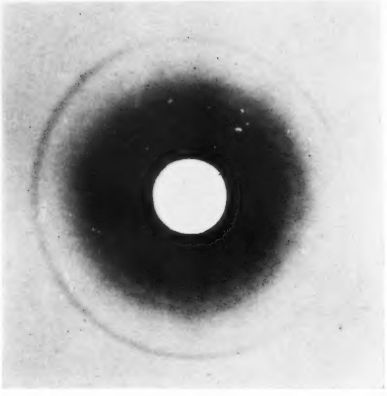


FIG. 11

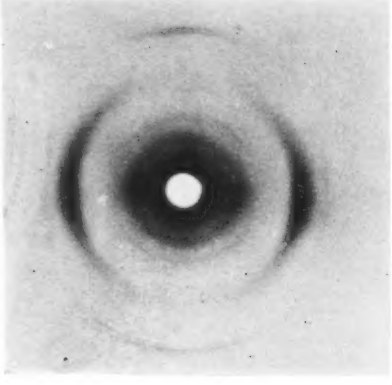
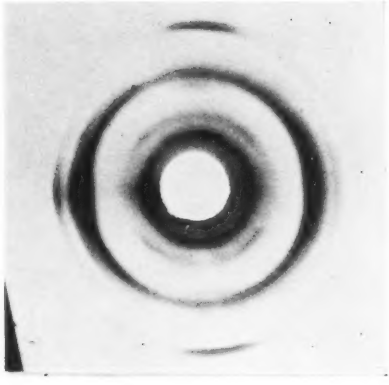


FIG. 12



MARIPOSITE FROM BELVADI, MYSORE STATE

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The occurrence of green quartzites as bands in the granites and gneisses to the N-W of Belvadi tank in the Sringeri Jahagir has been noted by the officers of the Mysore Geological Department (R. Bruce Foote, 1897; S. Lakshmana Rao, 1934). These quartzites are being used as ornamental stones on account of their hard and compact nature and pleasing appearance. The brilliant green mica contained in these rocks has been referred to as a chrome-bearing potash type, namely, fuchsite, possibly on account of its green colour; and consequently the rocks have been termed fuchsite quartzites. This green mineral has not so far been investigated in detail. A preliminary optical investigation of the mineral was undertaken a few months ago by the present writers, as a result of which, it was identified as chrome-phengite (Chakrapani Naidu and Mohamed Khan, 1955). Further work involving a chemical study of the mineral has been done and the results of both the optical and chemical investigations are recorded below:—

Optical Characters

The mineral, under study, shows the following optical properties:—

The relief is distinct with serrated borders. It shows straight extinction and is distinctly pleochroic with the following scheme:—

X = pale greenish blue

Y = yellowish green

Z = dark bluish green

$X < Y < Z$

It is optically negative with the optic plane $\perp$ (010) and $(-)\ 2V = 32°$, as determined on the Federov's Universal stage. The refractive indices of the mineral are:—

$\alpha = 1{\cdot}558$ (by calculation from β, γ and 2V)

$\beta = 1{\cdot}595$ (by immersion method)

$\gamma = 1{\cdot}598$ (by immersion method)

$\gamma - \alpha = 0{\cdot}040$ (from the indices)

The optical characters of the mineral are found to be very similar to those of the chrome-micas—fuchsite and mariposite, (Whitmore, Berry and Hawley, 1946, pp. 13 and 14), as recorded in Table I.

TABLE I

Locality	2V	Indices			
		α	β	γ	$\gamma-\alpha$
1. Belvadi mineral	32°	1·558	1·595	1·598	0·040
2. Fuchsite from Mashishimala, South Africa	35°	1·563	1·596	1·598	0·035
3. Fuchsite from new Consort mine, South Africa ..	36°	..	1·596	1·600	..
4. Mariposite from Mother lode, California	2E=36°	1·56	..	1·60	0·040
5. Mariposite from Rawhide mine, California	12°	1·565	1·601	1·605	0·040
6. Mariposite from Washington ..	40°	..	..	1·63	..

It is seen from the above table that the optical characters of the mineral, under study, are in fair agreement with those of fuchsites and mariposites.

CHEMICAL COMPOSITION

The chemical analysis of the Belvadi mineral* is given in Table II as calculated in atomic proportions on the basis of (O, OH, F) = 48 atoms and is compared with similarly calculated analyses of fuchsite and mariposite (Whitmore, Berry and Hawley, 1946, p. 11).

It is seen from the above table that the analysis of the mineral, under study, shows lower contents of Cr_2O_3 and Al_2O_3 and higher SiO_2 than the corresponding oxides of fuchsite. On the other hand it corresponds fairly well with similar oxides of mariposites. The aluminium-silicon ratio in the

* Analyst : C. N. Govinda Rao.

TABLE II

	1	2	3	4
SiO_2 ..	54·10	45·97	55·35	56·00
Al_2O_3 ..	25·51	31·67	25·62	23·52
Fe_2O_3 ..	0·62	2·56	0·63	3·30
Cr_2O_3 ..	0·98	4·81	0·18	0·78
FeO ..	1·01	0·53	0·92	0·51
MgO ..	3·18	0·31	3·25	2·12
CaO ..	Tr	0·15	0·07	0·37
Na_2O ..	Tr	1·03	0·17	2·72
K_2O ..	9·65	9·07	9·29	7·03
H_2O ..	4·54	3·99	4·52	3·52
TOTAL ..	99·59	100·09	99·95	99·87

	1		2		3		4	
Si ..	14·29	16·00	12·43	16·00	14·43	16·00	14·85	16·00
Al ..	7·92		10·09		7·89		7·35	
Fe''' ..	0·13	8·02	0·52	8·31	0·12	7·94	0·66	7·97
Cr ..	0·19		1·03		0·04		0·16	
Fe'' ..	0·22		0·12		1·26		0·84	
Mg ..	1·27		0·12		1·26		0·84	
Ca ..	..	3·26	0·04	3·70	0·02	3·16	0·11	3·89
Na ..	..		0·54		0·06		1·40	
K ..	3·26		3·12		3·08		2·38	
OH ..	7·98	48·00	7·19	48·00	7·85	48·00	6·22	48·00
O ..	40·02		40·81		40·25		41·78	

1. Belvadi mineral.
2. Fuchsite from Manitoba.
3. Mariposite from California.
4. Mariposite from Ross mine, Ontario.

tetrahedral group of the analysed mineral is 2: 14. Similar ratios calculated for fuchsite and mariposite from the analyses of Table II are 4: 12 (fuchsite)

and 2 : 14; 1 : 15 (for mariposite). In the aluminium-silicon ratio, the Belvadi mineral resembles mariposite more than fuchsite.

Fuchsite and mariposite are two types of Chrome-micas belonging to the muscovite family in which muscovite, ferri-muscovite and phengite are the end members (Winchell, 1951, p. 368). The first type, namely, fuchsite, being rich in muscovite molecule, has the structural formula closely approaching that of muscovite, *i.e.*, 2 $[K_2Al_4\ (Al_2Si_6)\ O_{20}\ (OH)_4]$, whereas the formula of the second type, namely, mariposite, being rich in phengite molecule, approaches that of phengite, *i.e.*, 2 $[K_2\ (Al, Mg, Fe'')\ (Al, Si_7)\ O_{20}\ (OH)_4]$ (Whitmore, Berry and Hawley, 1946, pp. 10 and 11).

In Table III is given the structural formula of the mineral, under study, as calculated from the atomic proportions on the basis of (O, OH, F) = 48 atoms and is compared with similar formulæ of fuchsites and mariposites, listed in Table II. For comparison is also given the ideal formula of phengite.

TABLE III

Belvadi mineral:

$2\ [(K, Na, Ca)_{1\cdot63}\ (Al, Mg, Fe''', Fe'', Cr)_{4\cdot01}\ (Al_{0\cdot85}Si_{7\cdot15})\ O_{20\cdot01}\ (OH)_{3\cdot99}]$

Fuchsite from Manitoba:

$2\ [(K, Na, Ca)_{1\cdot85}\ (Al, Mg, Fe''', F'', Cr)_{4\cdot15}\ (Al_{1\cdot78}Si_{6\cdot22})\ O_{20\cdot40}\ (OH)_{3\cdot59}]$

Mariposite from California:

$2\ [(K, Na, Ca)_{1\cdot58}\ (Al, Mg, Fe''', Fe'', Cr)_{3\cdot97}\ (Al_{0\cdot78}Si_{7\cdot22})\ O_{20\cdot07}\ (OH)_{3\cdot92}]$

Mariposite from Ontario:

$2\ [(K, Na, Ca)_{1\cdot58}\ (Al, Mg, Fe''', Fe'', Cr)_{3\cdot98}\ (Al_{0\cdot58}Si_{7\cdot42})\ O_{20\cdot89}\ (OH)_{3\cdot11}]$

Phengite:

$2\ [K_2\ (Al, Mg, Fe'')_4\ (Al, Si_7)\ O_{20}\ (OH)_4]$

It is seen from the above table that the structural formula of the Belvadi mineral is very similar to that of mariposite closely approaching the ideal formula of phengite and differs from the formula for fuchsite.

CONCLUSION

In the light of the above studies, it is evident that the green mica from Belvadi, though resembling fuchsite in its optical characters, does not correspond to it in chemical composition. On the other hand, it closely resembles mariposite, a typical chrome-phengite, from the type locality, Mariposa Estate in California (Whitmore, Berry and Hawley, 1946, p. 4). Hence it is concluded that the Belvadi mineral is not fuchsite but mariposite.

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INTENSITY MEASUREMENTS OF ULTRASONIC DIFFRACTION ORDERS

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1. Introduction

Bär (1953) was the first to study the intensity variation of diffraction orders with various parameters and compare the results with diffraction theories. Korff (1936), Neumann (1939) and Sanders (1936) studied the intensity variation employing the photo-cell with a d.c. amplifier. Except for qualitative observations by these authors, no systematic intensity measurements over a frequency range, especially at higher frequencies, are available in the literature.

The aim of this study is to present a precise method for and the results of measuring intensities of diffraction orders in the range 3 to 170 Mc/s employing a 931–A photo-multiplier tube which has a gain of 2,000,000 with an applied voltage of 125 volts per stage.

2. Method of Measurement

The method consists in setting up a photo-multiplier tube described above for intensity measurements. The high frequency order obtained by the usual Debye and Sear's diffraction method, is made to be incident on the photo-cathode through a narrow rectangular slit, the slit and the photo-tube being movable transversely across the diffraction pattern. The resulting photo-current is measured by means of a very sensitive mirror galvanometer, the deflections of which are proportional to the intensity of the diffraction order. To check the validity of this method, the variation of intensity of diffraction orders at 3·8 Mc/s with the angle of incidence is measured and the experimental results have shown satisfactory agreement with Raman and Nath's theory for oblique incidence. Accordingly, this technique is employed for obtaining the experimental data presented and discussed in the following section.

3. Experimental Results and Discussion

Two aspects of high frequency diffraction have been studied. The length of the sound field forms an important parameter in all the intensity

expressions derived in various diffraction theories. A measurement of the intensity of diffraction of the first order by varying the length of the sound field is, therefore, made. The experimental results, showing this variation of intensity with the length of the sound field, have been plotted in Fig. 1 (*a*). David (1937), basing himself on Brillouin's work, has developed a theory which predicts maximum and minimum of intensities for $1_{\pm 1}$ in the normal incidence position for specific values of the length of the sound field given by the expression $L = n \cdot \frac{\mu_0 \lambda^{*2}}{\lambda}$, where L is the length of the sound field traversed by light of wavelength λ; μ_0 and λ^* are the refractive index and sound wavelength in the liquid respectively and n is an odd integer for maximum and even integer for minimum of intensity. These positions of maxima and minima of the high frequency diffraction line could be detected very easily by the help of the photo-tube. The positions of maxima have not so far been observed by any of the investigators whereas the minima were observed visually by Rao (1948). A one-inch square X-cut quartz plate with a fundamental of 1·2 Mc/s is used to generate ultrasonics in carbon tetrachloride. The positions of successive maxima are expected to occur at values of L = 0·4, 1·2 and 2·0 cm. at a frequency of 23·0 Mc/s. These values agree fairly well with the values obtained by experiment as can be seen in Fig. 1 (*a*).

In the oblique incidence position, however, the behaviour of 1_{+1} and 1_{-1} is very much different from that of $1_{\pm 1}$ in the normal position. The nature of increase in intensity with the length of the sound field of either 1_{+1} or 1_{-1} is parabolic, while the increase of 1_{+1} is far more rapid than that of 1_{-1} as shown in Fig. 1 (*b*) for carbon tetrachloride at 23·0 Mc/s. The maximum intensity of the first order of diffraction, obtained from David's theory, is given by $1_m = \frac{(\pi \mu L)^2}{\lambda^2}$, which shows that the intensity of the first order increases as the square of the length of the sound field. This theoretical conclusion is very much in agreement with the experimental observations plotted in Fig. 1 (*b*).

The only point regarding which there is a discrepancy is that while the theory expects the intensity of the first order at normal incidence to go through minima of zero intensity, the experimental curve [Fig. 1 (*a*)] shows no such behaviour. The diffraction order never disappears and this deviation, however, could not be accounted for by the theory, which assumes an ideal sound field with undamped amplitude.

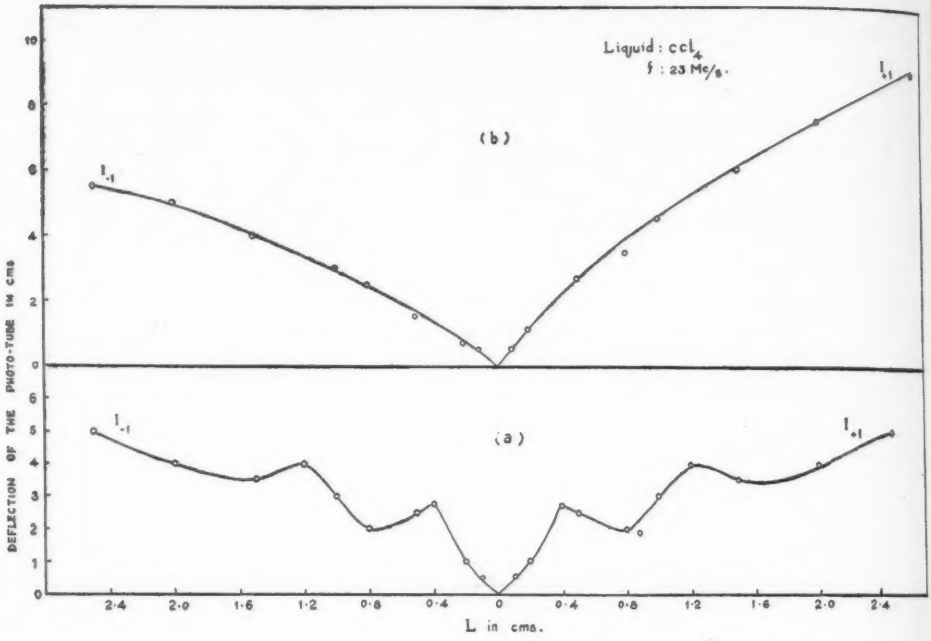

FIG. 1

The second aspect of interest of high frequency diffraction is to study the dependence of sharpness of diffraction on the parameter $\frac{\pi L}{\lambda^*}$. Observations are made with the photo-tube on high frequency diffraction produced in two common liquids, water and acetone in the frequency range 23·0 Mc/s to 164·0 Mc/s in the former and 23·0 Mc/s to 150 Mc/s in the latter. At lower frequencies upto 80·0 Mc/s, when sufficient power is used, both 1_{+1} and 1_{-1} orders are simultaneously present in the normal incidence position and persist over a large range of tilt of the crystal holder. At higher frequencies, however, the first order lines on both sides are never present simultaneously. In this investigation, special arrangements are made to reduce the power supplied to the crystal at moderate frequencies to such an extent that the first order diffraction lines at their appropriate Bragg angles are as weak as those obtained at the highest frequency. The crystal holder is to be tilted carefully to the appropriate angle, which is found to be in agreement with the value derived from the Bragg relation $\frac{\lambda}{\lambda^*} = 2\mu \sin\theta$,

so that the high frequency diffraction order makes its appearance. A further tilt from this position by as small an angle as 2·2′ in water at 164 Mc/s and 2·0′ in acetone at 150 Mc/s, results in complete disappearance of the order. The sharpness of diffraction is more in acetone than that in water. B. R. Rao obtained similar results, while studying this phenomenon qualitatively in water by making visual estimates. The experimental and theoretical curves showing this effect in water are presented in Fig. 2 for various frequencies. It will be noticed that the curves become sharper as one approaches higher frequencies, showing their dependence on the above parameter $\frac{\pi L}{\lambda^*}$.

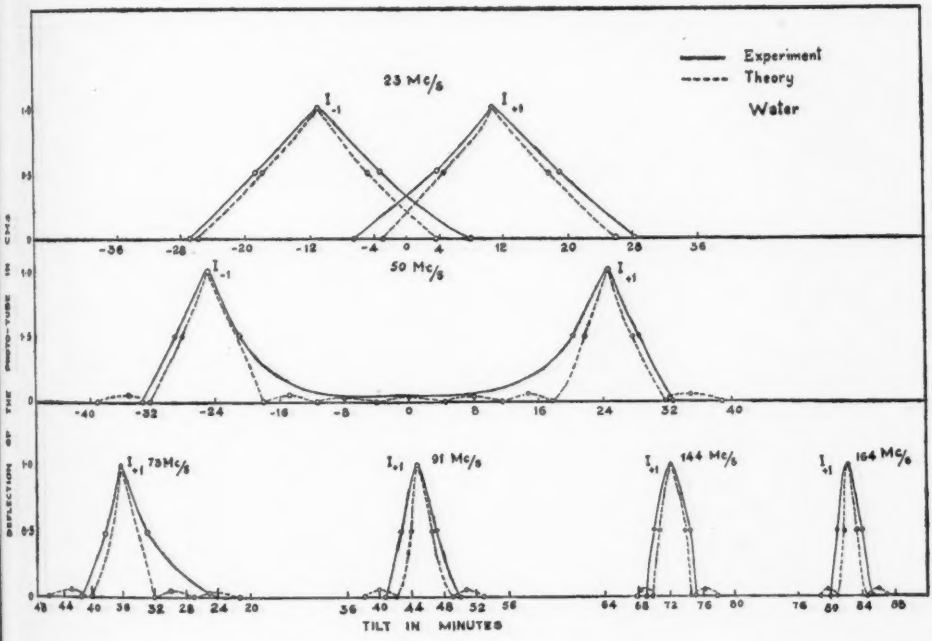

FIG. 2

4. SUMMARY

Quantitative intensity measurements on very high frequency ultrasonic diffraction orders in the range 3 to 170 Mc/s have been made for the first time employing a modern photo-multiplier tube. This method of measurement has proved far superior to other intensity measuring techniques described

in the literature. Two important aspects of high frequency diffraction have been studied and explained in the light of Brillouin's theory.

It is a pleasure to express my grateful thanks to Professor S. Bhagavantam for suggesting this problem and giving constant encouragement during the entire progress of this work.

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